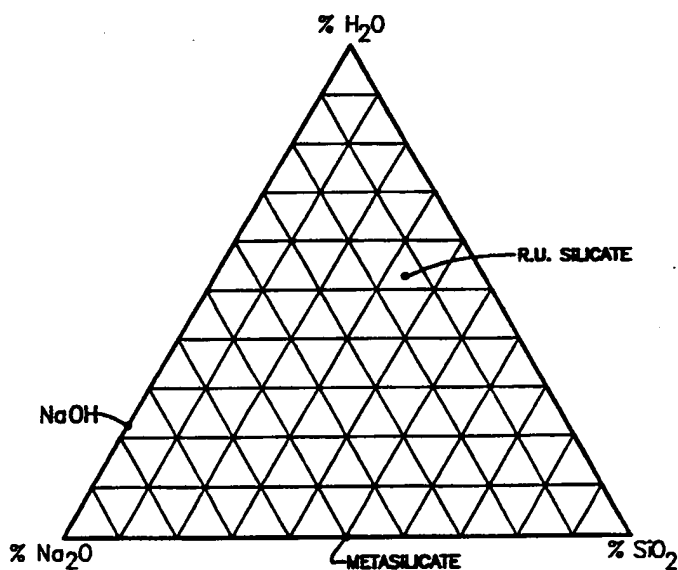




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b>  <b>C11D 17/00, 3/08, 3/37</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 92/13061</b>  <b>(43) International Publication Date:</b> <b>6 August 1992 (06.08.92)</b>
<b>(21) International Application Number:</b> PCT/US92/00492  <b>(22) International Filing Date:</b> 21 January 1992 (21.01.92)  <b>(30) Priority data:</b> 647,534                      29 January 1991 (29.01.91)      US  <b>(71) Applicant:</b> ECOLAB INC. [US/US]; Ecolab Center, Saint Paul, MN 55102 (US).  <b>(72) Inventors:</b> OLSON, Keith, E. ; 13942 Eveleth Court, Apple Valley, MN 55123 (US). OAKES, Thomas, R. ; 7816 North Demontreville, Lake Elmo, MN 55042 (US). TALLMAN, Daniel, N. ; 1840 West Country Road C-2, Roseville, MN 55113 (US). MIZUNO, William, G. ; 2925 Regent Avenue North, Golden Valley, MN 55422 (US).		<b>(74) Agents:</b> BYRNE, Linda, M. et al.; Merchant, Gould, Smith, Edell, Welter & Schmidt, 1000 Norwest Center, 55 East Fifth Street, Saint Paul, MN 55101 (US).  <b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK, DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), NO, SE (European patent).  <b>Published</b> <i>With international search report.          Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

**(54) Title:** PROCESS FOR MANUFACTURING CAST SILICATE-BASED DETERGENT**(57) Abstract**

A process for producing a solid cast silicate-based cleaning compositions which includes the step of combining appropriate concentrations of an alkali metal silicate, an alkali metal hydroxide and a source of water to form a reaction mixture that solidifies into a reaction product which is processable at temperatures below the melting point or decomposition temperature of the reaction product. The process provides for the rapid manufacture of a solid cast alkaline cleaning composition without melting of the cast composition. Incorporation of appropriate amounts of a combination of a polyacrylate and a phosphonate into the cleaning composition cooperate with the silicate present in the composition to form a threshold system which is effective for controll-

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	R	Romania
CF	Central African Republic	JP	Japan	RU	Russian Federation
CG	Congo	KP	Democratic People's Republic of Korea	SD	Sudan
CH	Switzerland	KR	Republic of Korea	SE	Sweden
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
DE	Germany	MC	Monaco	TC	Togo
DK	Denmark			US	United States of America

- 1 -

PROCESS FOR MANUFACTURING  
CAST SILICATE-BASED DETERGENT

5

Field of the Invention

The invention relates to solid, cast, silicate-based detergent compositions, methods of manufacturing such compositions, and threshold systems useful in such  
10 compositions. Specifically, the invention relates to methods of manufacturing substantially uniformly dispersed, solid, cast, silicate-based, alkaline detergent compositions which do not require "melting" of any component the reaction mixture or the reaction product and  
15 which can include an effective threshold system.

Background of the Invention

The advent of solid cast detergent compositions has revolutionized the manner in which detergents are dispensed by commercial and institutional entities which routinely  
20 use large quantities of cleaning solution. Prior to the advent of solid cast detergents, commercial and institutional entities were limited to either liquid, granular or pellet forms of detergent. However, because of the numerous unique advantages offered by solid cast  
25 detergents, the solid cast detergents, such as those disclosed in U.S. Patent Nos. Re. 32,763, Re. 32,818, 4,680,134 and 4,595,520 quickly replaced the conventional liquid and granular detergents in the commercial and institutional markets.

30 The unique advantages offered by solid cast detergents include improved handling resulting in enhanced safety, elimination of component segregation during transportation and storage, increased concentration of active ingredients within the composition, and various others.

35 One method of manufacturing solid cast detergent compositions involves the steps of forming a homogenous

- 2 -

melt of the detergent composition, casting the molten melt into a mold, and solidifying the melt by cooling.

Fernholz et al., U.S. Reissue Patent No. 32,763 describes a method of manufacturing a solid cast detergent composition which involves the steps of (i) forming an aqueous solution of two hydratable chemicals, such as sodium hydroxide and sodium tripolyphosphate, (ii) heating the solution to a temperature of about 65° to 85°C, (iii) increasing the concentration of hydratable chemicals in the heated solution to produce a solution which is liquid at the elevated temperature but will solidify when cooled to room temperature, and (iv) casting the heated solution into molds for cooling and solidification.

While the solid cast detergents manufactured in accordance with the molten processes constitute a significant improvement over the previously known liquid and granular detergent compositions, the molten process is time consuming, requires large quantities of energy, and can result in deactivation of desirable operative cleaning components incorporated into the detergent such as bleaches, defoaming agents, enzymes, and tripolyphosphates if processing parameters are not closely monitored.

One effort to simplify and improve the molten process is disclosed in Copeland, et. al., U.S. Patent No. 4,725,376 The Copeland patent describes a method of manufacturing a solid cast alkaline detergent composition capable of decreasing the extent of deactivation resulting from the manufacturing process. Briefly, the process disclosed by Copeland involves pouring an aqueous melt of a hydratable, alkaline, detergent component into a mold containing solid particles of a thermally-deactivatable detergent component such that the aqueous melt percolates through the interstitial void volume between the solid particles and then solidifies to form a solid cast

- 3 -

detergent composition containing homogeneously dispersed granules of the thermally-deactivatable detergent.

Gansser, U.S. Patent No. 4,753,755, discloses a method for producing a solid alkaline detergent composition  
5 similar in mechanism to Fernholz et al.

Smith, U.S. Patent No. 2,164,092, discloses a method for solidifying an aqueous alkaline solution by incorporating a metaphosphate into the alkaline solution under conditions capable of converting the metaphosphate to  
10 an orthophosphate and/or pyrophosphate with accompanying dehydration and solidification of the aqueous mixture.

While the processes disclosed by Gansser and Smith provide for the manufacture of solid cast detergent compositions, the process of Gansser additionally results  
15 in reaction mixtures which generally take several hours to solidify and require prolonged agitation to prevent segregation while the process of Smith is limited to phosphate-based detergents.

Accordingly, a substantial need exists for additional  
20 manufacturing techniques which can provide for the formation of solid cast detergent compositions without requiring the attainment of melt/decomposition temperatures.

#### Summary of the Invention

25 The invention is broadly directed to a cast solid composition and methods for the production of solid cast silicate-based cleaning compositions which do not require melt phase processing. Specifically, the invention provides for the production of solid cast silicate-based  
30 cleaning compositions which rapidly solidify substantially simultaneously across the entire cross section of the reaction product. In the process, as a result of mixing and under conditions of mixing, a thermodynamically unstable liquid mixture is formed that can rapidly solidify  
35 into a thermodynamically stable solid. Because the

- 4 -

cleaning composition includes silicate as the source of alkalinity, a synthetically effective threshold system may be incorporated into the composition for the purpose of preventing the precipitation of both calcium and magnesium ions.

The process combines appropriate concentrations of an alkali metal silicate or mixtures of silicates, an alkali metal hydroxide and a source of water to create a liquid or fluid reaction mixture which is processable at temperatures below the melting point or decomposition temperature of the reaction product and which forms a reaction product which is solid under processing conditions.

The product of the process of the invention typically comprises a hydrated silicate containing composition or mixtures of a hydrated silicate species thereof. The hydrated silicate materials can contain additional amounts of concentrated sodium hydroxide as part of the solid matrix. In the solidification processes involved in the invention, a silicate composition, optionally another silicate species, and sodium hydroxide, interact with a wash chemical to form a liquid reaction mixture that is thermodynamically unstable which becomes thermodynamically stable through a solidification process. In the solidification process, the materials react to alter the normally fluid constituent ratios to different ratios that are normally solid at ambient temperatures. In such reactions, we have found that most processing mixtures with common ratios of ingredients, that two or more discrete hydration states are formed in the reaction product. We have found that the production of two or more hydration states can be characteristic of products made with this reaction. It should be understood that at certain "perfect" ingredient ratios, single hydration states can be formed. However, under most processing conditions and combinations of ingredients, two, three or more, discrete

- 5 -

hydration states can be formed. Such hydration states can be identified using differential scanning calorimetry (DSC) wherein each hydration has its characteristic temperature on a DSC curve, each hydration having a peak in the curve at differing temperatures.

#### Definitions

As used herein, including the claims, the term "ambient" refers to those temperatures (about 10°C to about 50°C) and pressures (about 700 to 900 mm Hg) typically encountered in the environment.

As used herein, including the claims, the term "cleaning composition" refers to multiple component substances which are useful in cleaning surfaces and substrates.

As used herein, including the claims, the term "cleaning solution" refers to an aqueous solution containing a sufficient quantity of a cleaning composition to be effective for cleaning surfaces and substrates.

As used herein, including the claims, the term "wash chemical" or "operative cleaning component" refers to components which can enhance the cleaning ability of a cleaning composition. Operative cleaning component includes specifically, but not exclusively: sources of alkali such as an alkali metal hydroxide, an alkali metal silicate, anti-redeposition agents, bleaches, enzymes, sequestrants, surfactants, and threshold agents or systems. When used in the claims, a wash chemical, when combined with a first form of silicate, refers to a second different silicate composition or form. In other words, the different silicate is a silicate that differs in  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio.

As used herein, including the claims, the terms "deactivate" and "deactivation" refer to a reduction or elimination in a useful chemical property or characteristic through chemical modification.

- 6 -

As used herein, including the claims, the term "melting point or decomposition temperature", refers to the temperature at which a solid substance begins to melt or decompose the hydrate e.g. evaporate or drive off water.

5 The solid silicate systems of this invention are considered to possess a melt temperature if they pass from a solid to a liquid at a temperature below the boiling point of water such that the water portion of the composition remains in the heated composition and are considered to possess a  
10 decomposition temperature if they melt at a temperature above the boiling point of water such that the water portion of the composition leaves the heated composition as steam.

As used herein, including the claims, the term  
15 "externally supplied heat" refers to the intentional addition of heat to a system from a separate and independent heat source such as steam and specifically excludes the addition of heat to a system caused by variances in ambient conditions and exothermic reactions  
20 occurring between reactants in the system.

As used herein, including the claims, the term  
"formulation" refers to the chemical composition or constitution of a substance. The formulation of a mixture is defined by the amount and composition of each  
25 ingredient.

As used herein, including the claims, the term  
"processable" means having sufficient fluidity or sufficiently low viscosity to be stirred, mixed, agitated, blended, poured, and/or molded in common industrial mixing  
30 equipment.

As used herein, including the claims, the term "process conditions" refers to the product temperatures and pressures encountered during processing.

As used herein, including the claims, the term  
35 "reaction mixture" refers to a mixture of reactants prior



- 7 -

to conversion of a meaningful proportion of the reactants to a reaction product.

As used her in, including the claims, the term "meaningful proportion", when used in connection with

5 "reaction mixture", means a proportion sufficient to perceptibly alter the physical characteristics of the mixture or to introduce a desirable cleaning property to the cast material such as detergency, hardness sequestering, soil anti-redeposition, etc.

10 As used herein, including the claims, the term "reaction product" refers to the composition resulting from completion of the solidification of a reaction mixture.

As used herein, including the claims, the term "room temperature" refers to the temperature typically maintained

15 in an environmentally controlled living space (about 15°C to about 32°C).

As used herein, including the claims, the term "solid" refers to a substance which will not flow perceptibly under moderate stress. Specifically, a cast substance is deemed

20 to be "solid" when the substance will retain the shape of the mold when removed from the mold.

As used herein, including the claims, the term "stoichiometric excess" refers to an amount of a chemical reactant which exceeds that necessary to convert all other

25 reactants to product based upon the quantitative chemical relationship of the reactants. For example, a combination of 10 moles of hydrogen and 4 moles of oxygen to form H<sub>2</sub>O includes a stoichiometric excess of 2 moles of hydrogen.

As used herein, including the claims, the term

30 "supercooled" refers to a condition of thermodynamic instability caused by the existence of a liquid system at a temperature below the freezing point of that system.

As used herein, including the claims, the term "thermodynamic stability" refers to a condition of

35 thermodynamic equilibrium.

- 8 -

As used herein, including the claims, the term "thermodynamically unstable" refers to a thermodynamic situation where either the physical or chemical state of a liquid system has not achieved thermodynamic equilibrium and the instability created by mixing liquid components is released by the solidification of the unstable liquid, and the gain or loss of a heat of solidification.

As used herein, including the claims, the term "threshold agent" or "threshold system" refers to those compounds or combination of compounds which exhibit the ability to prevent the precipitation of hardness ions from an aqueous system at a concentration which is significantly less than the concentration of hardness ions in the aqueous system.

As used herein, the term "wt% water" refers to all water contained in the composition and specifically includes both free and chemically bound water regardless of source.

As used herein, the term "wt%" is based upon the amount of alkali metal silicate, alkali metal hydroxide and water in the reaction mixture unless otherwise specified.

#### Brief Description of the Drawings

FIGURE 1 is a ternary diagram depicting the  $H_2O$ ,  $Na_2O$  and  $SiO_2$  composition of selected reagents used in Experimental Trials 30-57 set forth in the Application.

FIGURE 2 is a portion of a ternary diagram depicting the  $H_2O$ ,  $Na_2O$  and  $SiO_2$  composition of the products obtained from Experimental Trials 30-57.

FIGURE 3 is a portion of a ternary diagram depicting the melting point or decomposition temperature of the products obtained from Experimental Trials 30-57 based upon the  $H_2O$ ,  $Na_2O$  and  $SiO_2$  composition of the product.

FIGURE 4 is a portion of a ternary diagram depicting the maximum processing temperatures achieved during Experimental Trials 30-57 based upon the  $H_2O$ ,  $Na_2O$  and  $SiO_2$

- 9 -

composition of the product.

FIGURE 5 is a portion of a ternary diagram depicting the  $\Delta T$  of the products obtained in Experimental Trials 30-57 based upon the  $H_2O$ ,  $Na_2O$  and  $SiO_2$  composition of the product.

FIGURE 6 is a portion of a ternary diagram depicting the solidification time of the products obtained in Experimental Trials 30-57 based upon the  $H_2O$ ,  $Na_2O$  and  $SiO_2$  composition of the product.

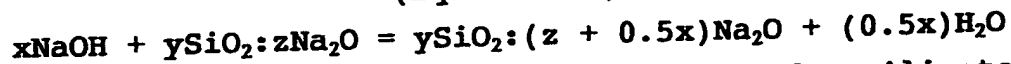
10                    Detailed Description of the Invention  
                         Including a Best Mode

A silicate-based alkaline cleaning composition which is solid under ambient conditions may be manufactured without heating the reaction mixture above the melt/decomposition  
15 temperature of the reaction mixture or reaction product by employing a solidification system including an alkali metal silicate, optionally, an alkali metal hydroxide, and water.  
Preferably, the alkali metal of the silicate and the alkali metal of the hydroxide are identical. An alkali metal  
20 silicate when reacted with another cast chemical, such as a different alkali metal silicate, and other optional wash chemicals, can become unstable in alkaline solution or suspension and can solidify. Because of low cost and ready availability, the sodium silicate and sodium hydroxide  
25 species are preferred. Accordingly, without intending to be limited thereby, the remainder of the specification will describe the invention in terms of sodium silicate and sodium hydroxide.

A mixture of a sodium silicate species and a second  
30 wash chemical such as a different sodium silicate, a phosphate, etc., with an amount of sodium hydroxide, can exothermically react in accordance with Equation 1 to increase the  $Na_2O$  content (alkalinity) of the silicate.

- 10 -

(Equation 1)



Controlled increases in the alkalinity of a silicate solution can transform the silicate solution from a system which is liquid under ambient conditions to a system which is solid under those same conditions.

Broadly, a substantially uniformly dispersed cleaning composition which is solid under ambient conditions may be manufactured without melting the reaction mixture or the reaction product by combining amounts of a sodium silicate or mixtures of silicates thereof, sodium hydroxide and water to achieve a reaction mixture containing about 20-45 wt% water and with an  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio of about 1:1 to 2.5:1; or amounts of sodium silicate or mixtures of silicates thereof, sodium hydroxide and about 20-50 wt% water and with an  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio of about 2.5:1 to 4:1. Specifically, a uniformly dispersed cleaning composition with a freezing point above about 70°C may be quickly and easily manufactured without melting the reaction mixture or the reaction product by combining amounts of a sodium silicate or mixtures of silicates thereof, sodium hydroxide and water to achieve a reaction mixture containing about 20-40 wt% water with an  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio of about 1.5:1 to 2.5:1 or amounts of sodium silicate or mixtures of silicates thereof, sodium hydroxide and about 20-45 wt% water and with an  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio of about 2.5:1 to 3.5:1.

Reaction mixtures with too much water do not readily form product which are solid at ambient conditions while mixtures with too little water are difficult to process because of their high viscosity. Reaction mixtures with an  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio which is too low have a melt/decomposition temperature which is too low to be of practical use while mixtures with an  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio which is too high do not readily form solids at ambient conditions and/or are difficult to manufacture without attaining melt/

- 11 -

decomposition temperatures due to a combination of the low melt/decomposition temperatures of the reaction mixtures and the high process temperatures required.

One of the reactants in the reaction mixture is an alkali metal. Commercial sodium silicates are available in both powdered and liquid forms. The powdered forms include both amorphous and crystalline powders in either hydrated or anhydrous form. The aqueous liquids are available with viscosities ranging from 0.5 to 600,000 cP at 20°C. The potassium silicates are sold either as a glass or an aqueous liquid. The synthetic lithium silicates typically are sold only as liquids.

Soluble silicates produce useful cleaning compositions as they are capable of maintaining a sufficiently high pH throughout the system due to their buffering ability and can perform certain basic detergent functions such as saponification of animal and vegetable oils and fats, emulsification of mineral oils, deflocculation of solid dirt particles, suspension of soils, prevention of redeposition of suspended dirt, and inhibition of soft metal corrosion by other ingredients in the cleaning composition.

A second reactant in the reaction mixture is sodium hydroxide. Sodium hydroxide or caustic soda is a white deliquescent solid. Anhydrous caustic soda is very soluble in water and highly alkaline with a melting point of 318.4°C, a density at 20°C of 2.130 g/ml, and a heat of fusion of 40.0 cal/gram. Figure 1 provides a general ternary diagram of silicon dioxide-sodium hydroxide-water systems.

A first obligatory consideration in selecting a reaction mixture formulation is the processability of the reaction mixture. Processability of the reaction mixture is dependent upon a number of factors including the concentration of solids, (silicate, hydroxide and optional

- 12 -

solid components) in the mixture [increased solids content decreases processability] and the temperature of the mixture [increased temperature increases processability].

Those reaction mixtures with a solids concentration of greater than about 80 wt% (water content of less than 20 wt%) are not readily processable because they are simply too thick to be properly mixed using standard mixing equipment. While it may be possible to process reaction mixtures having less than about 20 wt% water using specialized processing equipment, it is preferred to manufacture the product using a water content in excess of about 20 wt% in order to avoid the problems inherent in processing such highly viscous mixtures.

As a general matter, those reaction mixture formulations which satisfy the obligatory considerations of processability and solidifiability pass through a temporary phase at which time they are highly processable.

A second obligatory consideration in selecting a reaction mixture formulation is solidification of the reaction product. Referring to Tables 6 and 7 and Figures 3 and 6, those reaction mixtures with an  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio of about 1.5:1 to about 4:1 and less than about 50 wt% water can form a reaction product which is solid under ambient conditions. In order to ensure that the reaction product remains solid during normal shipping, storage and use conditions, the reaction product should be able to remain solid up to at least 50°C and preferably up to at least 65°C. In other words, the reaction product should have a melting point or a decomposition temperature of at least 50°C and preferably at least 65°C.

An elective consideration in selecting a reaction mixture formulation is the rate at which the reaction mixture solidifies. Preferably, the reaction mixture solidifies within about 1 minute to about 1 hour, most preferably within about 2 to 30 minutes, after combination

- 13 -

of the reactants. Reaction mixtures which solidify too quickly do not provide sufficient processing time and may result in a stratified reaction product and/or solidify prior to casting while those which solidify too slowly tend to retard the rate of production and/or permit separation of the individual components through settling unless a thickening agent is used.

Referring to Table 7 and Figure 6, the rate at which the reaction mixture solidifies generally appears to increase (solidify faster) as the  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio increases and as the water content decreases. While not all the data correlates precisely with these stated general trends, the differences can be attributed to a certain extent to the subjective nature of the assessment as to when the reaction mixture solidified.

Referring to Table 7 and a combination of Figures 5 and 6, the rate at which the reaction mixture solidifies also appears to be driven by the thermodynamic instability of the resultant reaction product as measured by the difference ( $\Delta T$ ) between the melt/decomposition temperature of the reaction product ( $T_{\text{melt}}$ ) and the actual physical temperature of the liquid reaction product ( $T_{\text{actual}}$ ). As a general principle, an increase in the thermodynamic instability of the reaction product ( $\Delta T$ ) causes an increase in the rate of solidification. In accordance with this general principle, the rate of solidification can be increased by producing a reaction product with a higher melting point or a decomposition temperature (increased  $T_{\text{melt}}$ ) and/or reducing the actual temperature achieved by the reaction mixture during processing (decreased  $T_{\text{actual}}$ ). In practice, the melting point or a decomposition temperature appears to affect the rate of solidification to a much greater extent than does the actual temperature. Without intending to limit the scope of the invention, the melting point or a decomposition temperature is believed to

- 14 -

control the rate of solidification because variations in the actual temperature are believed to cause offsetting effects in the rate of solidification by changing the  $\Delta T$  of the system and inversely changing the speed of molecular interactions within the reaction mixture/product.

A second elective consideration in selecting a reaction mixture formulation is the hardness of the completely solidified reaction product. Preferably, the reaction product is sufficiently hard that the cast product will not deform to any observable extent when subjected to the force of gravity for extended periods such as might occur during dispensing of the reaction product in a spray-type dispenser. Most preferably, the reaction product is sufficiently hard that the cast product may be removed from the mold and handled without support. Based upon the penetrometer data set forth in Table 7, the hardness of the completely solidified reaction product appears to increase with decreasing water content.

A third elective consideration in the selection of a reaction mixture formulation is the maximum temperature attained by the reaction mixture due to the exothermic reaction between the silicate, the hydroxide and the water. An exothermic reaction which raises the actual temperature above the melt/decomposition temperature of the reaction mixture and/or reaction product eliminates the benefits derived from producing the reaction product without attaining melt/decomposition temperatures. Accordingly, the reaction mixture should be formulated to prevent an exothermic reaction which would cause the reaction mixture or the reaction product to melt. In other words, the melt/decomposition temperature of the reaction product ( $T_{\text{melt}}$ ) should be greater than the maximum processing temperature attained by the reaction mixture and/or reaction product ( $T_{\text{max}}$ ) and is preferably greater by at least 10°C.



- 15 -

If desired, the maximum processing temperature attained by the reaction mixture and/or reaction product can be decreased by prereacting a portion of the reactants, cooling the prereaction product, and then employing the cooled prereaction product in the reaction mixture. Experimental Trials 18, 23, 25, 26, 29 and 30 demonstrate the use of this prereaction step by neutralizing Bayhibit PB AM<sup>®</sup> with sodium hydroxide prior to introduction of the Bayhibit PB AM<sup>®</sup> into the reaction mixture. The extent to which reactants can be prereacted is limited by the requirement that the prereaction product must be processable. The prereaction product must be capable of being dispersed throughout the final reaction mixture so as to be substantially uniformly intermixed within the resultant solid reaction product.

A final elective consideration in the selection of a reaction mixture formulation is the solubility of the completely solidified reaction product. The reaction product must be dissolved or otherwise dispersed in water to be effective. Therefore, the formulation and means of dispensing the reaction product must be capable of delivering the reaction product into a water supply at a reasonable rate. The reaction product could be dissolved prior to use to assure a ready supply of cleaning solution. However, such a dispensing system eliminates many of the advantages offered by solid cast compositions. To satisfactorily perform in most institutional and commercial dispensers of cleansing solutions, the reaction product should be capable of readily dissolving directly from the solid form at a rate of about 10 to 50 grams of active components (silicate, hydroxide and additional operative cleaning components) per minute, most preferably about 15 to 35 grams of active components per minute. The rate of dissolution depends upon several variables, including (i) formulation of the reaction product, (ii) method of

- 16 -

dispensing the reaction product, (iii) shape of the solidified reaction product, (iv) amount of surface area contact between reaction product and solvent, (v) solvent temperature, (vi) solvent flow rate, and (vii) solvent pressure. These variables may be independently adjusted to obtain the desired dispensing rate.

Because the reaction product remains below the melt/decomposition temperature and solidifies so quickly, it is believed that the silicate contained in the solidified reaction product is present in various hydrated forms depending upon the final sodium oxide:silicon dioxide ratio in the reaction product, the presence of other reactants and the availability of water during processing.

Operative cleaning components may be added to the reaction mixture formulation as desired in order to enhance a particular cleaning property or characteristic so long as the component(s) does not significantly interfere with solidification of the reaction mixture formula. A particularly effective operative cleaning component useful in the silicate-based alkaline detergent composition of this invention for holding or suspending divalent and trivalent hardness ions in the wash water and thereby reducing spotting, filming and liming of the washed surface is a threshold system including a combination of a polyacrylate and an organic phosphonate. As demonstrated in Tables 10 through 24, this threshold system cooperates in a synergistic fashion with the silicate-based detergent composition to effectively suspend both calcium and magnesium hardness ions.

The preferred polyacrylate has a molecular weight of about 2,000 to 7,000 such as Acrysol LMW-45ND<sup>®</sup>, a granular polyacrylic acid having an average molecular weight of about 4,500 available from the Rohm and Haas Company. Polyacrylates with a molecular weight of less than about 2,000 and more than about 7,000 are significantly less

- 17 -

effective as evidenced by Tables 12, 14, 16, 17, 18, and 20.

Preferred organic phosphonates include Dequest 2010, a 1-Hydroxyethylidene-1,1-diphosphonic acid, available from Monsanto, and Bayhibit PB AM<sup>®</sup>, a 2-phosphonobutane - 1,2,4 -tricarboxylic acid, available from the Mobay Corporation.

A detailed discussion of suitable phosphonates is provided in commonly owned U.S. Patent No. 4,846,993 issued to Lentsch et al. which is hereby incorporated by reference.

A ratio of about 2 to 6 parts polyacrylate to 1 part phosphonate is preferred at a loading of about 0.2 to 2 parts threshold system (polyacrylate and phosphonate) to 1 part silicate.

The alkali metal silicate, alkali metal hydroxide and water are preferably combined by adding the alkali metal hydroxide to an aqueous solution of the alkali metal silicate. The alkali metal silicate may be added to an aqueous solution of the alkali metal hydroxide but is less preferred because solid alkali metal silicates have a low dissolution rate in alkali metal hydroxide solutions.

The reaction mixture may be blended using both batch and continuous mixers with continuous mixers preferred for convenience. Substantially any standard mixer can be employed without difficulty.

The reaction mixture should be agitated until the components are uniformly dispersed throughout the mixture and then quickly cast in order to minimize solidification within the mixer. Self cleaning, continuous mixers which can provide effective mixing with residence times of less than about 20 seconds are preferred in order to reduce solidification of product within the mixer.

The reaction mixture may be cast into a temporary mold from which it is subsequently transferred for packaging or

- 18 -

may be cast directly into the packaging receptacle. Preferably, the reaction mixture is cast directly into the packaging container in order to eliminate the transfer step.

5       The packaging container may be made from any material capable of housing the highly caustic reaction mixture and reaction product including such materials as glass, steel, polyethylene, polypropylene, cardboard and cardboard composites. When the reaction mixture is cast directly  
10 into the container, the container must be capable of withstanding the temperatures encountered during the process due to the exothermic reaction between the alkali metal silicate, alkali metal hydroxide and water (about 40° to about 105°C). The container may be rigid or flexible.  
15 Because of its low cost and ability to structurally withstand chemical contact with the alkaline composition and processing temperatures of up to about 80°C, the container is preferably a rigid or flexible container constructed from a polyolefin such as polyethylene.

20       Since the reaction product solidifies substantially simultaneously throughout the entire cross section without the need to cool the product, the product may be cast into any desired size and shape.

      The reaction product is preferably dispensed from a  
25 spray-type dispenser such as those disclosed in U.S. Patent Nos. 4,826,661, 4,690,305, 4,687,121, and 4,426,362. Briefly, a spray-type dispenser functions by impinging a water spray upon an exposed surface(s) of the solid block of material so as to dissolve a portion of the material  
30 and then immediately directing the solution out of the dispenser to a reservoir or directly to a point of use. Table 5 provides an indication of the solubility of two reaction products in two different spray-type dispensers.

- 19 -

Experimental Procedure  
(Trials 1-29)

The reactants identified in Table 1 were placed into a polypropylene container equipped with a laboratory agitator in accordance with the sequence set forth in Table 2 to form a reaction mixture. The reaction mixture was agitated as set forth in Table 3 and then allowed to solidify at room temperature. The temperature attained by the reaction mixture due to an exothermic reaction between the reactants is also provided in Table 3. Specifics as to the rate of solidification and the physical characteristics of the solidified product are provided in Table 4.

Testing Procedures  
Penetrometer

The product was tested with a Precision Penetrometer, manufactured by GCA Precision Scientific, using a #73520 needle, also manufactured by GCA Precision Scientific. Time of testing noted in Table 4 represents the time between completion of reaction product agitation and commencement of the testing.

- Step 1 - Raise the penetrometer needle and scale connecting rod to their maximum height.
- Step 2 - Position the product directly underneath the penetrometer needle.
- Step 3 - Adjust the height of the entire needle-retention block to position the point of the needle immediately above the surface of the product.
- Step 4 - Start the machine and permit the penetrometer needle to penetrate into the test specimen for 5 seconds, plus or minus 0.2 seconds.
- Step 5 - Record the distance traveled by the penetrometer needle to the nearest millimeter.
- Step 6 - Repeat the procedure at a different position on the surface of the product to obtain 3 measurements.

- 20 -

Step 7 - Average the 3 measurements to obtain the p netrometer hardness factor of the product.

5                    Differential Scanning Calorimeter

The product was tested with a Perkin/Elmer DSC-7 Differential Scanning Calorimeter equipped with a Perkin/Elmer 3700 Data Station, a Perkin/Elmer TAC 7/3 Instrument Controller and a Perkin/Elmer Graphics Plotter

10    2. The tests were conducted in accordance with the operating instructions provided with the equipment employing the "parameters" and "conditions" set forth below.

	<u>Parameters</u>	<u>Conditions</u>
15	T Final: 200.0°C	End Conditions: L
	T Start: 20.0°C	Load Temp: 20.0°C
	T Min: 20.0°C	Go to Temp Rate: 200.0
	Scanning Rate: 10.0(°C/min)	Valve 1 Time: 0.0
	Y Range: 10.0	Valve 2: 0.0
20	Sample Wt: (3-7mg)	Delay Time: 0.0
	Baseline Status: N	Y Initial: 50
	Multitasking: N	

25        The test samples (3-7mg) were sealed in a stainless steel capsule using a Perkin/Elmer quick Press equipped with a Spacer Die. The reference capsule employed in the procedure was a stainless steel capsule which had been sealed empty.

Legend

- 30    Acrysol LMW-45        Polyacrylic acid having an average molecular weight of 4,500 in a 50% aqueous solution available from the Rohm and Haas Company.
- 35    Acrysol LMW-45ND     Granular polyacrylic acid having an average molecular weight of 4,500 available from the Rohm and Haas Company.

- 21 -

	Acrysol LMW-10N	An aqueous solution of average molecular weight of 1,000 available from Rohm and Haas Company. (Abbreviated LMW 10N)
5	Acrysol LMW-100N	An aqueous solution of polyacrylic acid having an average molecular weight of 10,000 available from Rohm and Haas Company. (Abbreviated LMW-100N).
10	Alcosperse 149 <sup>TM</sup>	A polyacrylate having an average molecular weight of about 2,000 available from Alco Chemical Company. (Abbreviated Alco 149)
15	Alcosperse 175 <sup>TM</sup>	A ring opened copolymer of acrylic acid and maleic anhydride having an average molecular weight of about 20,000 available from Alco Chemical Company. (Abbreviated Alco 175)
20	Belsperse 161 <sup>TM</sup>	A 50% aqueous solution of a polyacrylate containing phosphono groups in the backbone which has a molecular weight of about 4,000 available from Ciba-Geigy. (Abbreviated Bels 161)
25		
	Goodright 7058D <sup>TM</sup>	Powdered salt of granular polyacrylic acid having an average molecular weight of about 6,000 available from B.F. Goodrich. (Abbreviated Gdright 7058D)
30		
	Cyanamer P-35 <sup>TM</sup>	A polyacrylamide available from American Cyanamide of Wayne, NJ. (Abbreviated Cyp35)
35		
	PAA <sup>1</sup>	A homopolymer of acrylic acid having an average molecular weight of about 5,000.
40		
	PAA <sup>2</sup>	A copolymer of acrylic acid and itaconic acid having an average molecular weight of about 8,000.
45		
	PAA <sup>3</sup>	A homopolymer of acrylic acid having an average molecular weight of about 10,000.
	DCDPP	1,5 -dicarboxy 3,3 -diphosphono pentane having a solids content of about 90%.
50	Bayhibit PB AM <sup>®</sup>	Aqueous solution of 2-phosphonobutane - 1,2,4 - tricarboxylic acid having a solids content of 45-50% available from

- 22 -

- the Mobay Corporation. (Abbreviated Byhbt).
- 5 Neutralized Bayhibit PB AM<sup>®</sup> Bayhibit PB AM<sup>(R)</sup> which has been neutralized with NaOH beads at a weight ratio of 1.35:1 Bayhibit to NaOH.
- 10 Dequest 2016<sup>®</sup> Aqueous solution of 1-hydroxyethylidene bis phosphonic acid tetra sodium salt available from Monsanto.
- 15 Dequest 2010<sup>®</sup> 60% active aqueous solution of 1-hydroxyethylidene-1,1-Diphosphonic acid available from Monsanto.
- 20 Neutralized Dequest 2010 Dequest 2010<sup>®</sup> which has been (i) neutralized with NaOH beads at a weight ratio of 2.14:1 Dequest to NaOH, (ii) screen ground, and (iii) vacuum dried.
- 25 Dowfax 3B2<sup>®</sup> Aqueous solution of Decyl (sulfophenoxy) benzene-sulfonic acid disodium salt and oxybis (decylbenzene sulfonic acid) disodium salt having a maximum active content of 47% available from Dow Chemical Company.
- 30 Chlorine Source Granular dichloroisocyanurate encapsulated with an inner coating of sodium sulfate and an outer coating of sodium octyl sulfonate manufactured by Ecolab, Inc. (See specification for manufacturing process.)
- 35 EO/PO Surfactant 1 Propylene oxide terminated ethylene oxide/propylene oxide block copolymer having a 1% solution cloud point at 85-90°F.
- 40 EO/PO Surfactant 2 Ethylene oxide/propylene oxide block copolymer having a 1% solution cloud point at 93-100°F.
- 45 EO/PO Surfactant 3 Propylene oxide modified nonionic EO/PO block surfactant having a 10% solution cloud point at 107-110°F.
- 50 Bz-EOx-R Benzyl ether of a polyethoxylated linear alcohol having a 1% solution cloud point at 60-64°F. made in accordance with the procedure set forth in U.S. Letters



- 23 -

Patent No. 3,444,242.

	LAS Flake <sup>®</sup>	Flak d alkyl benzene sulfonate available from Stepen Company.
5	Neodol 25-7 <sup>®</sup>	Mixture of C <sub>12-15</sub> alcohol ethoxylates available from Shell Chemical Company.
10	NPE 9.5	Polyethylene glycol ether of nonyl phenol having an average of 9.5 moles ethylene oxide per mole of nonyl phenol.
15	Pluronic RA40 <sup>®</sup>	Alkoxylated fatty alcohol from BASF Wyandotte Corporation - Chemicals Division.
20	RU Silicate <sup>®</sup>	Sodium silicate solution having an Na <sub>2</sub> O:SiO <sub>2</sub> weight ratio of about 0.4:1.0 and a solids content of 47.05% available from the PQ Corporation.
	Triton CF-21 <sup>®</sup>	An alkylaryl polyalkoxylate available from Rohm and Haas Corporation.
25	Versene 220 <sup>®</sup>	Powdered EDTA available from Dow Chemical Company.
	NTA	Nitrilotriacetic acid monohydrate available from Monsanto.
30	Powdered Tripolyphospate	Tripolyphosphate having a particle size which provides at least 95% passage through a 60 mesh screen, and at least 90% passage through a 100 mesh screen.
35	Granular Tripolyphosphate	Tripolyphosphate having a particle size which provides at least 99.5% passage through a 12 mesh screen, at least 88% passage through a 20 mesh screen, and less than 5% passage through a 200 mesh screen.
40		
45	Large Granular Tripolyphosphate	Tripolyphosphate having a particle size which provides at least 98% passage through an 8 mesh screen, less than 10% passage through a 30 mesh screen, and less than 5% passage through a 100 mesh screen.

TABLE 1Composition of Trials  
(grams)

	<u>Trl #1</u>	<u>Trl #2</u>	<u>Trl #3</u>	<u>Trl #4</u>	<u>Trl #5</u>	<u>Trl #6</u>
! Silicat	32.8	32.8	32.8	32.8	32.8	32.8
odium M tasillicate	10.5	10.5	10.5	10.5	10.5	10.5
odium Hydroxid Bead	26.2	26.2	26.2	26.2	26.2	26.2
it r						
<u>REFRACTANT/BUILDERS</u>						
rysol LMW						
rysol LMW-45ND <sup>®</sup>						
rysol LMW-100N <sup>®</sup>						
hibit PB AM <sup>®</sup> Neut						
quist 2010 <sup>®</sup>						
quist 2016 <sup>®</sup>						
utralized Dequest <sup>®</sup>	4.0	4.0	4.0	4.0	4.0	4.0
owfax 3B2 <sup>®</sup>						
PO Surfactant 1	10.0					
PO Surfactant 2						
PO Surfactant 3						
-EOx-R <sup>®</sup>		10.0				
S Flake <sup>®</sup>						
odrit 7058ND <sup>™</sup>	12.7		10.0			
odol 25-7 <sup>®</sup>		12.7	12.7	12.7	12.7	12.7
PE 9.5						
luronic RA40 <sup>®</sup>						
citon CF-21 <sup>®</sup>						
ars n 220 <sup>®</sup>						
TA						
ower d/TPP						
n Granular/TPP						
y Granular/TPP						
<u>LEACH</u>						
olab Chlorine						
<u>ILLUENT</u>						
odium Chloride						

TABLE 1 (continued)

	<u>Trl #7</u>	<u>Trl #8</u>	<u>Trl #9</u>	<u>Trl #10</u>	<u>Trl #11</u>	<u>Trl #12</u>
U Sillicat	1389.2					
odium Metasilicate	445.3	521.3	481.3	1312.0	1392.6	34.4
odium Hydroxid Bead	1269.7	167.2	154.4	420.7	533.0	11.0
at r		476.9	440.3	1200.2	1274.0	31.5
<u>URFACANT/BUILDERS</u>						
crisol LMW			218.0			9.5
crisol LMW-45ND <sup>®</sup>		144.0				
crisol LMW-100N <sup>®</sup>						
ayhibit PB AM <sup>®</sup> Neut						
equ st 2010 <sup>®</sup>			54.4			
equst 2016 <sup>®</sup>						
neutraliz d Dequest <sup>®</sup>	103.5	39.0		138.2		2.6
owfax 3B2						
O/PO Surfactant 1	37.8	13.6	13.6	48.6	37.3	0.9
O/PO Surfactant 2						
O/PO Surfactant 3						
z-EOx-R <sup>®</sup>						
AS Flak <sup>®</sup>						
oodrit 7058ND <sup>™</sup>	386.4			512.3	395.0	
odol 25-7 <sup>®</sup>						
PE 9.5						
luronic RA40 <sup>®</sup>						
riton CF-21 <sup>®</sup>						
ers n 220 <sup>®</sup>						
TA						
ow r d/TPP						
m Granular/TPP						
g Granular/TPP						
<u>LEACH</u>						
colab Chlorine						10.0
<u>ILUENT</u>						
odium Chlorid						

TABLE 1 (continued)

	<u>Trl #13</u>	<u>Trl #14</u>	<u>Trl #15</u>	<u>Trl #16</u>	<u>Trl #17</u>	<u>Trl #18</u>
Silicat	32.2	457.3	487.0	487.0	492.0	168.6
ium M tasilicat	10.3	146.7	156.2	156.2	157.8	54.1
ium Hydroxide Bead	29.4	418.4	445.5	445.5	450.0	154.2
er						
<u>FACTANT/BUILDERS</u>						
ysol LMW						
ysol LMW-45ND <sup>®</sup>	12.7	192.0	190.2	190.2	192.1	
ysol LMW-100N <sup>®</sup>				13.7		
hibit PB AM <sup>®</sup> Neut						46.2
u st 2010 <sup>®</sup>						
quest 2016 <sup>®</sup>		129.5				
itraliz d Dequest <sup>®</sup>	3.4		51.4	51.4	51.9	
ifax 3B2 <sup>®</sup>			13.7			
/PO Surfactant 1	1.2	18.1	18.0	18.0	18.2	6.1
/PO Surfactant 2						
/PO Surfactant 3						
-EOx-R <sup>®</sup>						
3 Flak						
odrite 7058ND <sup>™</sup>						
odol 25-7 <sup>®</sup>						
3 9.5						
ironic RA40 <sup>®</sup>						
iton CF-21 <sup>®</sup>						
rsen 220 <sup>®</sup>						
A						
w r d/TPP						
Granular/TPP						
Granular/TPP						
EACH						
olab Chlorin	10.7					
LUENT						
dium Chlorid						

70.5

27

TABLE 1 (continued)

	<u>Trl #19</u>	<u>Trl #20</u>	<u>Trl #21</u>	<u>Trl #22</u>	<u>Trl #23</u>	<u>Trl #24</u>
Sillicat	399.4	399.4	389.2	723.3	818.4	818.4
lum M tasillicat	128.1	128.1	124.8	234.8	262.4	262.4
lum Hydroxide B ad	365.4	365.4	365.0	670.0	748.7	748.7
er						
<u>FACTANT/BUILDERS</u>						
ysol LMW						
ysol LMW-45ND <sup>®</sup>	45.0	45.0	68.0	82.4	352.3	352.3
ysol LMW-100N <sup>®</sup>						
hibit PB AM <sup>®</sup> Neut					231.9	
1 st 2010 <sup>®</sup>						
est 2016 <sup>®</sup>						
traliz d Dequest <sup>®</sup>						
fax 3B2 <sup>®</sup>						
PO Surfactant 1	7.2	7.2	7.2	13.3	27.6	27.6
PO Surfactant 2					55.7	55.7
PO Surfactant 3						
EOx-R <sup>®</sup>						
Flake <sup>®</sup>						
irite 7058ND <sup>™</sup>						
tol 25-7 <sup>®</sup>						
9.5						
conic RA40 <sup>®</sup>						
lon CF-21 <sup>®</sup>						
s n 220 <sup>®</sup>						
er d/TPP	416.8	416.8	416.8			
granular/TPP						
granular/TPP						
ACH						
lab Chlorin						
JENT						
ium Chloride						231.9

TABLE 1 (continued)

	<u>Trl #25</u>	<u>Trl #26</u>	<u>Trl #27</u>	<u>Trl #28</u>	<u>Trl #29</u>
ilicat	818.4	830.7	733.1	733.1	374.0
um M tasilicat	262.4	266.4			
um Hydroxide B ad	748.7	759.9	844.3	844.3	1258.6
r			145.4	145.4	224.4
<u>ACTANT/BUILDERS</u>					
sol LMW		352.0			352.0
sol LMW-45ND <sup>®</sup>					
sol LMW-100N <sup>®</sup>					
ibit PB AM <sup>®</sup> Neut	231.9	232.3			232.3
est 2010 <sup>®</sup>					
est 2016 <sup>®</sup>					
raliz d D qu st <sup>®</sup>					
ax 3B2 <sup>®</sup>					
o Surfactant 1			25.1	25.1	55.7
o Surfactant 2	27.6				
o Surfactant 3	55.7				
ox-R <sup>®</sup>					
Flak					
rit 7058ND <sup>™</sup>					
ol 25-7 <sup>®</sup>					
9.5					
onic RA40 <sup>®</sup>					
on CF-21 <sup>®</sup>		55.7			
sen 220 <sup>®</sup>			749.2		
er d/TPP				749.2	
granular/TPP					
granular/TPP					
ACH					
lab Chlorin					
UENT					
ium Chlorid	352.3				

29

TABLE 2  
Order of Addition

	<u>Trl #1</u>	<u>Trl #2</u>	<u>Trl #3</u>	<u>Trl #4</u>	<u>Trl #5</u>	<u>Trl #6</u>
Silicat	1	1	1	1	1	1
lium M tasilicate	6	6	6	6	6	6
lium Hydroxide Bead	3	3	3	3	3	3
FACTANT/BUILDERS						
ysol LMW						
ysol LMW-45ND <sup>®</sup>						
ysol LMW-100N <sup>®</sup>						
hibit PB AM <sup>®</sup> Neut						
u st 2010 <sup>®</sup>						
uest 2016 <sup>®</sup>						
utraliz d Dequest <sup>®</sup>	4	4	4	4	4	4
fax 3B2						
'PO Surfactant 1	2					
'PO Surfactant 2						
'PO Surfactant 3						
EOx-R <sup>®</sup>		2				
i Flak			2			
idrit 7058ND <sup>™</sup>		5	5		5	5
idol 25-7 <sup>®</sup>	5			5	2	
i 9.5						
ronic RA40 <sup>®</sup>						
.ton CF-21 <sup>®</sup>						
s ne 220 <sup>®</sup>						
er d/TPP						
Granular/TPP						
Granular/TPP						
ACH						
lab Chlorine						
UENT						
lium Chlorid						

30

TABLE 2 (continued)

	<u>Trl #7</u>	<u>Trl #8</u>	<u>Trl #9</u>	<u>Trl #10</u>	<u>Trl #11</u>	<u>Trl #12</u>
Silicate	1	1	1	1	1	1
ium M tasilicate	5	5	6	6	4	4
ium Hydroxide Bead	2	2	2	2	2	2
FACTANT/BUILDERS						
ysol LMW			4			4
ysol LMW-45ND <sup>®</sup>		6				
ysol LMW-100N <sup>®</sup>						
hibit PB AM <sup>®</sup> N ut						
uest 2010 <sup>®</sup>			5			
uest 2016 <sup>®</sup>						
utraliz d D qu st <sup>®</sup>	4	4		4		4
ifax 3B2						
'PO Surfactant 1	3	3	3	3	3	3
'PO Surfactant 2						
'PO Surfactant 3						
-EOx-R <sup>®</sup>						
i Flak						
odrit 7058ND <sup>™</sup>						
odol 25-7 <sup>®</sup>	6			5	4	
9.5						
ronic RA40 <sup>®</sup>						
iton CF-21 <sup>®</sup>						
sene 220 <sup>®</sup>						
r d/TPP						
Granular/TPP						
Granular/TPP						
EACH						
lab Chlorin						
UENT						
ium Chloride						5



TABLE 2 (continued)

	<u>Trl #13</u>	<u>Trl #14</u>	<u>Trl #15</u>	<u>Trl #16</u>	<u>Trl #17</u>	<u>Trl #18</u>
Silicat	1	1	1	1	1	1
dium M tasilicate	4	5	5	5	4	4
dium Hydroxid Bead	3	2	2	2	2	4
it r						
REFRACTANT/BUILDERS						
tycol LMW	4	6	5	5	4	
tycol LMW-45ND <sup>®</sup>						
tycol LMW-100N <sup>®</sup>						
yhibit PB AM <sup>®</sup> Neut						
quest 2010 <sup>®</sup>						3
qu st 2016 <sup>®</sup>						
utraliz d D quest <sup>®</sup>	4	4				
wfax 3B2 <sup>®</sup>			5	5	4	4
/PO Surfactant 1	2	3	4	3	3	2
/PO Surfactant 2						
/PO Surfactant 3						
-EOx-R <sup>®</sup>						
S Flak <sup>®</sup>						
odrite 7058ND™						
odol 25-7 <sup>®</sup>						
E 9.5						
uronic RA40 <sup>®</sup>						
iton CF-21 <sup>®</sup>						
rs n 220 <sup>®</sup>						4
A						
w r d/TPP						
Granular/TPP						
Granular/TPP						
EACH						
clab Chlorine	5					
LUENT						
dium Chlorid						

TABLE 2 (continued)

	<u>Trl #19</u>	<u>Trl #20</u>	<u>Trl #21</u>	<u>Trl #22</u>	<u>Trl #23</u>	<u>Trl #24</u>
illicat	1	1	1	1	1	1
um Metasilicate	3	3	4	3	4	3
um Hydroxid B ad2	2	2	2	2	2	2
x						
ACTANT/BUILDERS						
sol LMW						
sol LMW-45ND <sup>®</sup>	3	3	3	3	4	3
sol LMW-100N						
ibit PB AM <sup>®</sup> Neut					3	
st 2010 <sup>®</sup>						
est 2016 <sup>®</sup>						
raliz d Dequ st <sup>®</sup>						
ax 3B2						
O Surfactant 1	1	1	1	1		
O Surfactant 2					1	1
O Surfactant 3					1	1
Ox-R <sup>®</sup>						
Flake						
rite 7058ND <sup>™</sup>						
ol 25-7 <sup>®</sup>						
9.5						
onic RA40 <sup>®</sup>						
on CF-21 <sup>®</sup>						
en 220 <sup>®</sup>						
red/TPP						
ranular/TPP	3	3	4	3		
ranular/TPP						
CH						
ab Chlorine						
IENT						
um Chlorid						3

33

TABLE 2 (continued)

	<u>Trl #25</u>	<u>Trl #26</u>	<u>Trl #27</u>	<u>Trl #28</u>	<u>Trl #29</u>
RU Silicate	1	1	1	1	1
Sodium M tasilicate	4	4			
Sodium Hydroxide Bead	2	2	3	3	3
Water			2	2	2
<u>SURFACTANT/BUILDERS</u>					
Acrysol LMW					
Acrysol LMW-45ND <sup>®</sup>		4			5
Acrysol LMW-100N <sup>®</sup>	4				
Bayhibit PB AM <sup>®</sup> Neut	3	3			
Dequ st 2010 <sup>®</sup>					
Dequest 2016 <sup>®</sup>					
Neutralized Dequest <sup>®</sup>					
Dowfax 3B2					
EO/PO Surfactant 1			1	1	1
EO/PO Surfactant 2	1				
EO/PO Surfactant 3	1				
Bz-EOx-R <sup>®</sup>					
LAS Flake <sup>®</sup>					
Goodrit 7058ND <sup>™</sup>					
Neodol 25-7 <sup>®</sup>					
NPE 9.5					
Pluronic RA40 <sup>®</sup>					
Triton CF-21 <sup>®</sup>		1			
V rsene 220 <sup>®</sup>			4		
NTA					
Powered/TPP				4	
Sm Granular/TPP					
Lg Granular/TPP					
<u>BLEACH</u>					
Ecolab Chlorine					
<u>DILUENT</u>					
Sodium Chloride	4				

- 34 -

TABLE 3Processing Data

<u>Trl #</u>	<u>Time*</u> <u>(min)</u>	<u>Temp</u> <u>(°F)</u>	<u>Rpm</u>	<u>Trl #</u>	<u>Time</u> <u>(min)</u>	<u>Temp</u> <u>(°F)</u>	<u>Rpm</u>
1	-	-	-	16	3.00	184	700
2	-	-	-	17	1.33	179	700
3	-	-	-	18	3.00	177	500
4	-	-	-	19	2.00	198	700
5	-	-	-	20	2.50	185	700
6	-	-	-	21	2.75	201	700
7	-	175 <sup>1</sup>	-	22	1.30	200	700
8	0	-	300	23	-	-	-
	2.58	179.6	400				
9	0	-	300	24	3.50	194	-
	4.00	-	400				
	14.00	-	500				
	22.00	200	500				
	23.50	191	500				
10	30.00	170	550	25	5.00	189	-
11	-	-	500	26	2.75	171	700
12	-	-	-	27	1.50	-	500
				2.00	-	500	
				5.00	195	-	
13	-	-	-	28	2.50	-	700
				3.00	-	700	
				6.00	204	-	
14	2.50	-	300	29	2.00	-	700
	3.25	172	300		2.50	165	700
15	1.00	-	700 <sup>2</sup>				
	3.00	183	900 <sup>3</sup>				

\* Timing initiated after addition of last component completed.

---

<sup>1</sup>Maximum temperature attained.

<sup>2</sup>Rpm during addition of components 1, 2 and 3.

<sup>3</sup>Rpm during addition of components 4 and 5.

- 35 -

TABLE 4Penetrometer Data

<u>Trl #</u>	<u>Time<sup>4</sup> (min)</u>	<u>Needle Depth (mm)</u>	<u>Comments</u>
1	-	-	Formed a completely hardened solid product.
2	-	-	Formed a completely hardened solid product.
3	-	-	Formed a completely hardened solid product.
4	-	-	Formed a completely hardened solid product.
5	-	-	Formed a completely hardened solid product.
6	-	-	Formed a completely hardened solid product.
7	-	-	Solidifies in less than 10 minutes.
8	1 4 8 12 16 20 24 28	329 142, 60, 36 4, 8, 12 3, 2, 4 2, 0, 3 0, 0, 0 2, 0, 0 2, 1, 8	Solidified in less than 10 minutes.
9	24 hrs	0, 0, 0	Product began to solidify immediately but thinned as the Dequest 2010 <sup>®</sup> was added. Formed thick surface skin immediately after completion of agitation.

---

<sup>4</sup>Time represents the length of time after all components have been added and agitation has been completed.

- 36 -

TABLE 4 (continued)

<u>Trl #</u>	<u>Time<sup>5</sup> (min)</u>	<u>Needle Depth (mm)</u>	<u>Comments</u>
10	-	-	Completely solidified when checked one hour after completion of agitation.
11	-	-	Surface solidified within 5 minutes after completion of agitation. Completely solid product removed from the mold 30 minutes after completion of agitation.
12	-	-	Formed a solid product.
13	-	-	Formed a solid product.
14	-	-	Product still pourable 30 minutes after completion of agitation. Completely solidified 90 minutes after completion of agitation.
15	-	-	Product is solid 1.5 minutes after completion of agitation and completely hardened 2.5 minutes after completion of agitation.
16	-	-	Product is solid 0.25 minutes after completion of agitation and removed from mold 15 minutes after completion of agitation.

---

<sup>5</sup>Time represents the length of time after all components have been added and agitation has been completed.

- 37 -

TABLE 4 (continued)

<u>Trl #</u>	<u>Time<sup>6</sup> (min)</u>	<u>Ne dle Depth (mm)</u>	<u>Comments</u>
17	-	-	Product is solid 1 minute after completion of agitation and completely hardened 4 minutes after completion of agitation.
18	8.0	34, 42, 36	Product is solid 12 minutes after completion of agitation and completely hardened 15-16 minutes after completion of agitation.
	12.0	4, 3, 2	
	16.0	2, 0, 0	
	20.0	0, 0, 0	
19	1.0	11, 3, 4	Difficult to incorporate component 3 premix due to thickness of silicate and caustic mixture.
	3.0	0, 0, 4	
	5.0	0, 0, 0	

---

<sup>6</sup>Time represents the length of time after all components have been added and agitation has been completed.

- 38 -

TABLE 4 (continued)

<u>Time<sup>7</sup></u> <u>Trl #</u>	<u>Needle</u> <u>Depth</u> <u>(min)</u>	<u>(mm)</u>	<u>Comments</u>
20	0 4.0 8.0	329 13, 5, 6 0, 0, 0	Component 3 premix readily incorporated into mixture of silicate and caustic.
21	0 4 8 12 16 20 24 28 32	329 329 329 329 247, 198, 278 183, 193, 161 145, 141, 132 121, 121, 115 126, 191, 121	
22	4	0, 3, 0	
23	-	-	Formed a completely hardened solid product.
24	-	-	Product solidified very quickly.
25	-	-	Formed a completely hardened solid product.
26	0 4 8 12 16 20	329 329 16, 18, 16 17, 9, 5 5, 4, 2 1, 2, 2	Product solidified about 16 minutes after after completion of
27	0 4 8	7, 3, 9 5, 1, 3 1, 2, 1	Product became very viscous one minute after completion of agitation and solidified very quickly.
28	4	0, 0, 0	Product solidified almost immediately after completion of agitation.

---

<sup>7</sup>Time represents the length of time after all components have been added and agitation has been completed.



- 39 -

TABLE 4 (continued)

<u>Time<sup>8</sup></u> <u>Trl #</u>	<u>Needle</u> <u>Depth</u> <u>(min)</u>	<u>(mm)</u>	<u>Comments</u>
29	0	329+	Product developed a tough skin about 25 minutes after completion of agitation with a viscous center. Appears to be solidifying from the outside towards the inside.
	4	329+	
	8	329+	
	12	329+	

---

<sup>8</sup>Time represents the length of time after all components have been added and agitation has been completed.

- 40 -

Experimental Procedure  
(Trials 30-57)

The reactants RU Silicate<sup>®</sup>, water, metasilicate and sodium hydroxide were sequentially placed into a polypropylene container equipped with a laboratory agitator to form a reaction mixture. The proportions of each reactant are set forth in Table 5. The reaction mixture was agitated and then allowed to solidify at room temperature. The maximum temperature attained by the reaction mixture due to an exothermic reaction between the reactants is provided in Table 6. A subjective assessment of the time at which the reaction product solidified is also provided in Table 6.

The decomposition/melt temperature of the solidified reaction product was determined using a Perkin-Elmer Differential Scanning Calorimeter. The hardness of the solidified reaction product was determined in accordance with the penetrometer testing procedure. The relevant data as to the decomposition/melt temperature and the hardness of the solidified reaction product are set forth in Table 6.

- 41 -

TABLE 5Compositions of Trials Establishing Phase Diagram

<u>Trl #</u>	<u>RU Si</u> <u>(g)</u>	<u>Meta Si</u> <u>(g)</u>	<u>NaOH</u> <u>(g)</u>	<u>H<sub>2</sub>O</u> <u>(g)</u>	<u>%SiO<sub>2</sub></u>	<u>%Na<sub>2</sub>O</u>	<u>%H<sub>2</sub>O</u>
30	44.73	14.35	40.92	0	21.91	45.20	32.89
31	27.37	17.84	54.73	0	17.82	55.34	26.84
32	34.90	10.83	54.27	3.28	16.38	50.73	32.89
33	27.41	13.23	59.36	7.49	14.52	52.58	32.89
34	24.83	11.99	653.18	8.24	13.06	54.04	32.89
35	22.71	10.96	66.33	8.86	11.88	55.23	32.89
36	47.79	21.14	31.31	0.77	26.27	40.84	32.89
37	37.01	33.30	28.98	0.70	28.67	44.51	26.82
38	30.77	27.69	40.01	1.53	23.84	49.34	26.82
39	22.95	13.47	63.11	0.47	14.25	58.93	26.82
40	60.04	7.80	31.82	0.33	23.78	36.94	39.28
41	51.34	5.56	40.00	3.09	19.80	40.91	39.29
42	38.35	4.18	49.67	7.80	14.79	45.92	39.28
43	44.59	0	51.28	4.13	14.81	45.91	39.28
44	35.64	0	56.71	7.65	11.84	48.88	39.28
45	33.77	0	53.75	12.47	11.22	46.33	42.45
46	42.29	0	48.59	9.13	14.04	43.51	42.45
47	56.48	0	39.97	3.55	18.76	38.79	42.45
48	62.56	3.71	31.49	2.24	22.60	34.95	42.45
49	37.53	0	51.47	11.00	12.46	45.09	42.45
50	48.41	0	44.87	6.72	16.06	41.53	42.40
51	40.41	0	46.44	13.15	13.42	41.58	45.00
52	38.21	0	43.90	17.90	12.69	39.31	48.00
53	32.34	0	58.72	8.94	10.74	49.98	39.28
54	30.66	0	55.65	13.69	10.18	47.37	42.45
55	29.29	0	53.18	17.52	9.73	45.27	45.00
56	38.21	0	43.90	21.90	12.20	37.79	50.00
57	37.53	0	51.47	15.63	11.91	43.09	45.00

- 42 -

TABLE 6Experimental Results

<u>Trl #</u>	<u>Max<sup>9</sup> Temp (°C)</u>	<u>Solid (Min)</u>	<u>Major DCS Peak (°C)</u>	<u>Minor DCS Peak (°C)</u>	<u>Penetrometer Needle Depth (mm)</u>		
30	86.1	2	141.4	62.9	1	4	2
31	65.6	20	164.5	42.5	0	2	0
32	86.7	30	178.8	54.8	1	0	0
33	83.3	26	176.5	39.6	0	0	1
34	73.9	22	50.4	--	4	1	0
35	70.0	48	62.7	--	0	3	0
36	76.7	12	83.2	--	0	0	0
37	71.1	6	72.5	105.0	0	1	1
38	87.2	1	173.2	27.0	4	0	1
39	62.2	3	60.9	--	0	0	0
40	87.8	16	85.0	--	0	1	0
41	95.0	21	108.1	69.6	0	3	0
42	91.1	1	159.2	--	5	1	3
43	92.8	1	159.6	--	8	3	0
44	100.0	720	161.0	--	5	2	2
45	104.4	720	171.5	23.0	22	14	24
46	95.0	6	144.0	--	36	27	16
47	96.1	720	81.4	--	0	0	0
48	97.2	720	80.3	--	0	0	0
49	95.6	2	157.2	--	6	9	8
50	96.1	10	100.5	72.4	2	2	5
51	98.9	12	103.0	53.6	329	329	329
52	103.3	47	112.6	64.4	329	329	329
53	99.4	44	40.4	183.5	0	0	0
54	105.0	--	23.0	178.6	329	329	329

---

<sup>9</sup>Maximum temperature attained by reaction mixture during processing.

- 43 -

TABLE 6 (continued)

<u>Trl #</u>	<u>Max<sup>10</sup> Temp (°C)</u>	<u>Solid</u>	<u>Major DCS Peak (°C)</u>	<u>Minor DCS Peak (°C)</u>	<u>Pen tromet r Needle Depth (mm)</u>
55	102.2	22	164.9	--	21 17 24
56	102.8	--	73.9	--	329 329 329
57	96.1	6	147.5	48.3	22 32 53

---

<sup>10</sup>Maximum temperature attained by reaction mixture during processing.

- 44 -

Experimental Procedure  
(Trials 60-75)

The powder premix portion of the formula as set forth in Table 7 was blended in a ribbon mixer. The liquid  
5 premix portion of the formula as set forth in Table 7 was blended in a mix tank with the RU silicate added first and the temperature of the liquid premix adjusted as set forth in Table 8.

The powder and liquid premixes were blended in a  
10 Teledyne-Readco continuous mixer with the powder premix fed through an Acrison portable volumetric feeder and the liquid premix fed through a Bran-Lubbe piston metering pump. The feed rate of the powdered and liquid premixes, the mixing rate and the temperature of the product upon  
15 exiting the T-R mixer are set forth in Table 8.

The Teledyne-Readco continuous mixer was equipped with  
24 sets of 2 inch diameter, lens-shaped paddles having variable shapes and configurations designed to achieve either forward or reverse conveying in combination with  
20 sheer conveying sections proximate to the inlet orifice to the mixture. The mixer provided close tolerance between the paddles and the jacket.

The rate at which a solidified product of Formulas #2 and #3 may be dispensed in a spray-type dispenser is set  
25 forth in Table 9.

- 45 -

TABLE 7Processing Formulas  
(wt)

	<u>Frml #1</u>	<u>Frml #2</u>	<u>Frml #3</u>	<u>Frml #4</u>
<u>Powder Premix</u>				
Sodium Metasilicate	10.6	10.6	10.5	10.5
Sodium Hydroxide Bead	30.3	27.3	30.0	27.1
Acrysol LMW-45ND	14.1	14.1	14.1	14.1
<u>Liquid Premix</u>				
RU Silicate	33.1	33.1	32.8	32.8
Sodium Hydroxide	--	2.9	--	2.9
Bayhibit PB AM Neut	9.3	9.3	9.3	9.3
EO/PO Surfactant 1	2.6	2.7	--	--
Surfactant 2	--	--	1.1	1.1
Surfactant 3	--	--	2.2	2.2

- 46 -

TABLE 8Processing Data

<u>Trial #</u>	<u>Formula #</u>	<u>Liquid (°C)</u>	<u>Feed Rate (kg/min)</u>	<u>Mix Rate (rpm)</u>	<u>End Temp (°C)</u>
60	1	26.7	3.74	116	63.3
61	1	26.7	3.74	220	63.9
62	1	26.7	7.48	158	62.2
63	1	26.7	7.48	220	63.9
64	2	54.5	3.74	116	58.9
65	2	54.5	3.74	220	60.0
66	2	26.7	3.74	116	45.0
67	2	26.7	3.74	220	47.2
68	3	54.5	3.74	116	77.5
69	3	54.5	3.74	220	77.2
70	3	54.5	7.48	158	71.1
71	3	54.5	7.48	220	76.7
72	4	54.5	7.48	158	48.9
73	4	54.5	7.48	220	50.0
74	4	26.7	7.48	158	48.3
75	4	26.7	7.48	220	48.3



- 47 -

Testing Procedures  
Dispensing Rate

The dispensing rates of the reaction products obtained from Trials #30 and #31 were tested in a Guardian System™ spray-type, detergent reservoir dispenser, manufactured by Ecolab, Incorporated under United States Patent No. 4,063,663 at a line pressure of 35 psig and a water temperature of 50-55°C in accordance with the procedure set forth below.

- 10        Step 1 - Weigh fresh capsule.
- Step 2 - Precondition composition by placing the capsule in the dispenser and contacting the exposed surface of the composition with a water spray for one minute.
- 15        Step 3 - Remove capsule from the dispenser and allow the capsule to stand inverted for one minute. Weigh any composition which drips from the capsule after removal of the capsule from the dispenser.
- 20        Step 4 - Weigh the capsule.
- 25        Step 5 - Replace capsule into the dispenser and dispense for one minute.
- Step 6 - Remove capsule from the dispenser and allow the capsule to stand inverted for one minute. Weigh any composition which drips from the capsule after removal of the capsule from the dispenser.
- 30        Step 7 - Weigh the capsule.
- 35        Step 8 - Calculate the initial dispensing rate by subtracting the sum of the weight of the capsule in step seven and the weight of the composition which dripped from the capsule in step six from the weight of the capsule in step four and then dividing the subtotal by one minute.
- 40        Step 8 - Replace capsule into the dispenser and dispense for four minutes.
- 45        Step 8 - Replace capsule into the dispenser and dispense for four minutes.

- 48 -

- 5      Step 9 - Remove capsule from the dispenser and allow the capsule to stand inverted for one minute. Weigh any composition which drips from the capsule after removal of the capsule from the dispenser.
- 10      Step 10 - Weigh the capsule.
- 15      Step 11 - Calculate the intermediate dispensing rate by subtracting the sum of the weight of the capsule in step ten and the weight of the composition which dripped from the capsule in step nine from the weight of the capsule in step seven and then dividing the subtotal by four minutes.
- 20      Step 12 - Replace capsule into the dispenser and dispense for four minutes.
- 25      Step 13 - Remove capsule from the dispenser and allow the capsule to stand inverted for one minute. Weigh any composition which drips from the capsule after removal of the capsule from the dispenser.
- 30      Step 14 - Weigh the capsule.
- 35      Step 11 - Calculate the final dispensing rate by subtracting the sum of the weight of the capsule in step fourteen and the weight of the composition which dripped from the capsule in steps six, nine and thirteen from the weight of the capsule in step ten and then dividing the subtotal by four minutes.
- 40      Step 12 - Calculate the overall dispensing rate by subtracting the sum of the weight of the capsule in step fourteen and the weight of the composition which dripped from the capsule in steps thirteen from the weight of the capsule in step four and then dividing the subtotal by nine minutes.

- 49 -

TABLE 9Dispensing Rate

	<u>Frml #</u>	<u>Initial (g/min)</u>	<u>Middle (g/min)</u>	<u>Final (g/min)</u>	<u>Average (g/min)</u>	<u>Nozzle Type</u>
5	2	163	132	106	124	1
	3	140	114	87	105	1
10	2	135	170	221	189	2
	2	116	169	205	179	2
	3	113	139	161	146	2
	3	102	127	167	142	2
	3	110	126	166	142	2
15	Nozzle Type 1 - Whirl Jet, one-eighth inch, model 8W, Wide Angle manufactured by Spraying Systems.					
20	Nozzle Type 2 - Full Cone, one-eighth inch, model 3.5, Narrow Angle manufactured by Spraying Systems.					

Precipitate Inhibition Test

- 25 Various combinations of polymeric organic acids and phosphonates were evaluated for their ability to control the precipitation of calcium and magnesium at threshold levels in accordance with the procedure set forth below.
- 30 Step 1 - Set hot water bath at 70° C and allow to equilibrate.
- 35 Step 2 - Wash five eight-ounce, wide-mouth, glass bottles with a 10% nitric acid solution, rinse with tap water, rinse with distilled water and then allow to air dry.
- 40 Step 3 - Prepare solutions of the organic acids, phosphonates, silicates and carbonates which are to be used in the test in separate volumetric flasks.

- 5 Step 4 - Test water for hardness in accordance with the hardness concentration test set forth below. Record the hardness of the water (control).
- 10 Step 5 - Label the bottle caps.
- 15 Step 6 - Place ninety-nine milliliters of the water in each bottle and then sequentially add the indicated amounts of threshold agent monomer(s), threshold agent polymer(s), sodium silicate, and sodium carbonate as set forth in Tables 10 through 24 using the appropriate stock solutions created in step three.
- 20 Step 7 - Adjust the pH of the solution in each bottle to between 11.4 to 11.6 by adding either about a 15% solution of NaOH or about a 15% solution of HCl as appropriate.
- 25 Step 8 - Tightly cap the bottles with the labeled caps, shake the bottles to facilitate dissolution of the added components, and then place the bottles in the water bath for 2 hours.
- 30 Step 9 - Withdraw approximately twenty milliliters of the solution in each bottle with a syringe and filter the withdrawn samples through a Millipore filter system (Catalog # SX00002500) manufactured by The Millipore Corporation using a Type HA Millipore filter having a 0.45 micron pore size. Place the filtrate into a correspondingly labeled test tube.
- 40 Step 10 - Test the five filtrate samples for concentrations of calcium, magnesium and sodium ions remaining in the solution in accordance with the hardness concentration test set forth below. Record the concentration of each ion in each solution.

## 45 Results

The data obtained are set forth in Tables 10 through 24. The test was repeated five times for each threshold system. Table 10 provides the details for each test while subsequent tables provide only the average of the five

- 51 -

tests for each system.

The data clearly demonstrates that a synergistic effect for controlling both calcium and magnesium is achieved by a combination of a polyacrylate of the proper molecular weight, a phosphonate-type compound and a silicate. Effective control of both of these ions is essential for obtaining good dishwashing results.

It should be noted that in this and all subsequent tables (Tables 10 through 24) all testing was done in the presence of 400 ppm of added  $\text{Na}_2\text{CO}_3$ . This is added to give a constant high level of carbonate to insure a high tendency for the precipitation of calcium carbonate.

#### Testing Procedure Cation Concentration Test

- 15 The individual concentrations of calcium, magnesium and sodium in the aqueous filtrates obtained in the precipitation test were obtained using a Leeman Labs Plasma Spec ICP in accordance with the standard protocol for operation of the unit and the procedures set forth below.
- 20 The concentrations of calcium and magnesium in the filtrates indicates the effectiveness of the various threshold systems to prevent precipitation of these ions. (The greater the concentration of ions in the filtrate the greater the effectiveness of the threshold system).
- 25 Because the samples generally contain a silicate, the samples may not be preserved as addition of a preservative acid causes the formation of a precipitate which interferes with the analysis. Accordingly, analysis of the samples was conducted by Inductively Coupled Plasma Spectroscopy
- 30 (ICP) within a few hours of filtration.

#### Preparation of Standardized Reagents

Prepare the standard individual solutions set forth below:

- 52 -

	Calcium	1000 ppm
	Magnesium	1000 ppm
	Sodium	1000 ppm
	HNO <sub>3</sub>	concentrated
5	HCl	concentrated

Prepare five standard mixed solutions for calibrating the ICP as set forth in Table A by (i) adding the indicated volume of each of the standard individual solutions to a one liter volumetric flask containing approximately 200 milliliters of Millipore DI water, (ii) adding 5.0 milliliters of the HNO<sub>3</sub> solution and 5.0 milliliters of the HCL solution to the volumetric flask, and then (iii) adding sufficient additional Millipore DI water to produce 1000 milliliters of standard mixed solution. These standards are stable for 2 months.

Table A

20	Standard Solution <sup>1</sup> Solution	Solution <sup>2</sup> (blank)	Solution <sup>2</sup> (ml)	Solution <sup>3</sup> (ml)	Solution <sup>4</sup> (ml)	Solution <sup>5</sup> (ml)
	Ca	0	1	10	50	100
	Mg	0	1	10	50	100
25	Na	0	10	50	150	300

Obtain an ampule containing a certified concentration from EPA, Cincinnati, Ohio and prepare as instructed. The prepared solution is to be used as a check standard (external).

Prepare an internal mixed solution in the same manner set forth for preparation of the standard mixed solutions using 40 milliliters of the Ca, 40 milliliters of the Mg, and 50 milliliters of the Na standard individual solutions. The prepared solution is also to be used as a check standard (internal).

53

TABLE 10

Precipitate Inhibition Test

Deq No. ppm	PAA <sup>1</sup> ppm	Sil <sup>1</sup> ppm	Carb ppm	Ca ppm	Mg ppm	Na ppm	pH*
Ctrl							
1	-	-	400		61.1	23.8	4.3
2	-	-	400	1.0	1.0	445	11.5
3	-	-	400	1.0	1.0	446	11.6
4	-	-	400	1.0	1.0	449	11.5
5	-	-	400	1.0	1.0	416	11.4
			400	1.0	1.0	477	11.6
Average				1.0	1.0	447	
6	60	400	400	58.1	22.4	530	11.4
7	60	400	400	56.1	21.7	528	
7	60	400	400	55.5	20.3	539	
8	60	400	400	56.5	21.6	535	11.4
9	60	400	400	52.4	18.9	509	11.4
10	60	400	400	56.2	21.2	531	11.4
Average				55.8	21.0	529	
11	60	-	400	43.8	18.5	465	11.5
12	60	-	400	46.3	22.0	410	
12	60	-	400	21.9	4.1	419	
13	60	-	400	47.1	22.5	419	11.3
14	60	-	400	48.0	22.1	432	11.4
15	60	-	400	46.7	20.9	425	11.3
Average				42.3	18.4	428	

54

<u>No.</u>	<u>Deg</u> <u>ppm</u>	<u>PAA</u> <sup>1</sup> <u>ppm</u>	<u>Si1</u> <sup>1</sup> <u>ppm</u>	<u>Carb</u> <u>ppm</u>	<u>Ca</u> <u>ppm</u>	<u>Mg</u> <u>ppm</u>	<u>Na</u> <u>ppm</u>	<u>pH</u> *
16	15	-	400	400	20.7	1.0	513	11.4
17	15	-	400	400	21.3	1.0	419	11.3
18	15	-	400	400	20.9	1.0	507	11.4
19	15	-	400	400	20.4	1.0	518	11.4
20	15	-	400	400	21.4	1.0	497	11.4
			Average		20.9	1.0	491	
21	-	60	400	400	14.2	23.3	542	11.5
22	-	60	400	400	14.7	23.6	538	11.5
23	-	60	400	400	14.7	23.6	522	11.4
24	-	60	400	400	14.8	23.7	515	11.4
25	-	50	400	400	14.8	23.4	533	11.5
			Average		14.6	23.5	530	
26	15	-	-	400	16.3	1.0	400	11.5
27	15	-	-	400	17.3	1.0	408	11.4
28	15	-	-	400	17.2	1.0	416	11.3
29	15	-	-	400	17.2	1.0	402	11.4
30	15	-	-	400	17.0	1.0	409	11.4
			Average		17.0	1.0	415	
31	-	60	-	400	11.7	22.7	469	11.5
32	-	60	-	400	11.8	22.9	460	11.5
33	-	60	-	400	11.8	23.1	451	11.4
34	-	60	-	400	12.0	23.0	455	11.4
35	-	60	-	400	11.9	22.8	454	11.4
			Average		11.8	22.9	458	



55

<u>No.</u>	<u>Deq</u> <u>ppm</u>	<u>PAA</u> <sup>1</sup> <u>ppm</u>	<u>Si1</u> <sup>1</sup> <u>ppm</u>	<u>Carb</u> <u>ppm</u>	<u>Ca</u> <u>ppm</u>	<u>Mg</u> <u>ppm</u>	<u>Na</u> <u>ppm</u>	<u>pH</u> *
36	-	-	400	400	2.1	10.9	522	11.5
37	-	-	400	400	2.3	13.3	539	11.5
38	-	-	400	400	1.8	8.2	542	11.5
39	-	-	400	400	2.2	14.7	541	11.5
40	-	-	400	400	2.3	14.4	546	11.4
			Average		2.1	12.3	538	

\* After Filtration

\*\* After 24 Hours

Conclusions

The concentration of threshold agents in the systems of Table 10 were selected to stress the system (calcium and magnesium barely being controlled when all three of the threshold agents were present). Much of the subsequent testing was done at higher levels of threshold agents so as to more accurately depict actual dishwashing use conditions.

Table 10 indicates:

- 10           The phosphonate (Dequest 2010™) is ineffective for suspending magnesium and suspends only one-fourth of the calcium at a concentration of 15 ppm when used alone.
- 15           The polyacrylate (PAA<sup>1</sup>) is effective for suspending magnesium but suspends only about one-fifth of the calcium at a concentration of 60 ppm when used alone.
- 20           The silicate (Sil<sup>1</sup>) is ineffective for suspending calcium and suspends only one-half of the magnesium at a concentration of 400 ppm when used alone.
- 25           A combination of phosphonate (Dequest 2010™) and silicate (Sil<sup>1</sup>) is ineffective for suspending magnesium and suspends only one-third of the calcium despite the fact that the silicate is capable of suspending one-half of the magnesium when used alone. The phosphonate appears to inhibit the ability of the silicate to suspend magnesium.
- 30           A combination of polyacrylate (PAA<sup>1</sup>) and silicate (Sil<sup>1</sup>) is effective for suspending magnesium but suspends only about one-fourth of the calcium despite the fact that the silicate is capable of suspending one-half of the magnesium when used alone.
- 35           A combination of phosphonate (Dequest 2010™), polyacrylate (PAA<sup>1</sup>) and silicate (Sil<sup>1</sup>) is effective for suspending magnesium and calcium. A sum of the
- 40
- 45

- 57 -

individual components would predict an ineffective suspension of magnesium (inhibitory effect of phosphonate upon silicate) and poor suspension of calcium.

5

It is noted for completeness that the results obtained from the binary system of a phosphonate and a polyacrylate was not included in the analysis as the silicate is a necessary component of the detergent composition into which the threshold system is employed and will therefore always be present.

TABLE 11

15	<u>Nos.</u>	<u>Deq. 2010</u> <u>ppm</u>	<u>PAA<sup>1</sup></u> <u>ppm</u>	<u>Sil<sup>1</sup></u> <u>ppm</u>	<u>Ca</u>	<u>Mg</u>	<u>pH</u>
	1-5	-	-	-	<1.0	<1.0	11.3
	6-10	20	-	-	23.0	.3	11.2
20	11-15	-	80	-	15.6	19.8	11.2
	16-20	-	-	400	1.4	10.0	11.3
	21-25	20	80	-	52.8	18.6	11.4
	26-30	-	80	400	15.7	21.0	11.3
	31-35	20	-	400	21.7	<1.0	11.3
25	36-40	20	80	400	51.7	20.91	11.4
	CONTROL				55.6	23.6	

Conclusions

30 Concentration of Dequest 2010™ and PAA<sup>1</sup> was increased with respect to the concentrations employed in Table 10. At these higher levels both the binary system of Dequest 2010™ and PAA<sup>1</sup> (Nos. 21-25) and the tertiary system of Dequest 2010™, PAA<sup>1</sup> and Sil<sup>1</sup> (Nos. 36-40) provide effective  
35 control. This would not be expected from the sum of the individual component tests.

- 58 -

TABLE 12

	<u>Nos.</u>	<u>Deq 2010</u> <u>(ppm)</u>	<u>LMW 10N</u> <u>(ppm)</u>	<u>LMW 100N</u> <u>(ppm)</u>	<u>PAA<sup>1</sup></u> <u>(ppm)</u>	<u>Ca</u> <u>(ppm)</u>	<u>Mg</u> <u>(ppm)</u>	<u>pH</u>
5	1-5	-	80	-	-	5.8	9.5	11.2
	6-10	-	-	80	-	11.3	20.5	11.4
	11-15	-	80	-	80	17.4	21.7	11.5
	16-20	20	80	-	-	30.0	<1.0	11.2
10	21-25	20	-	80	-	39.3	10.5	11.3
	26-30	20	-	-	80	54.8	20.4	11.2
	31-35	20	60	-	20	30.2	1.3	11.3
	35-40	20	-	60	20	47.5	14.9	11.3
15	CONTROL					59.9	22.3	

Conclusions

A polyacrylate having an average molecular weight of about 1000 (LMW 10N™) provides significantly poorer calcium control and slightly poorer magnesium control than obtained with a polyacrylate having an average molecular weight of about 5,000 (PAA<sup>1</sup>) when used alone.

A polyacrylate having an average molecular weight of about 10000 (LMW 100N™) provides significantly poorer calcium control and about the same magnesium control as obtained with a polyacrylate having an average molecular weight of about 5,000 (PAA<sup>1</sup>) when used alone.

Addition of a phosphonate (Dequest 2010™) to the low molecular weight polyacrylate (LMW 10N™) and the high molecular weight polyacrylate (LMW 100N™) results in a decrease in the ability of the polyacrylate to control magnesium. This is not observed when Dequest 2010™ is added to the intermediate molecular weight polyacrylate (PAA<sup>1</sup>).

35

- 59 -

TABLE 13

	<u>Nos.</u>	<u>ByHbt</u> <u>ppm</u>	<u>PAA<sup>1</sup></u> <u>ppm</u>	<u>Sil<sup>1</sup></u> <u>ppm</u>	<u>Ca</u>	<u>Mg</u>	<u>pH</u>
5	1-5	-	-	-	<1.0	<1.0	11.2
	5-10	20	-	-	43.7	1.8	11.3
	11-15	-	80	-	14.0	19.5	11.3
	16-20	-	-	400	1.4	13.1	11.3
10	21-25	20	80	-	56.5	21.1	11.1
	26-30	-	80	400	13.7	20.1	11.0
	31-35	20	-	400	31.4	1.0	11.1
	36-40	20	80	400	54.8	20.1	11.0
15	CONTROL				56.8	21.0	

Conclusions

The phosphonate Bayhibit PB AM™ (2-phosphonobutane-1,2,4-tri-carboxylic acid), performs substantially the same as Dequest 2010™.

TABLE 14

	<u>Nos.</u>	<u>Deq</u> <u>2010</u> <u>(ppm)</u>	<u>PAA<sup>1</sup></u> <u>(ppm)</u>	<u>PAA<sup>2</sup></u> <u>(ppm)</u>	<u>PAA<sup>3</sup></u> <u>(ppm)</u>	<u>Sil<sup>1</sup></u> <u>(ppm)</u>	<u>Ca</u> <u>(ppm)</u>	<u>Mg</u> <u>(ppm)</u>	<u>pH</u>
25	1-5	10	40	-	-	400	38.7	10.5	11.6
	6-10	10	-	40	-	400	27.5	1.8	11.5
30	11-15	10	-	-	40	400	27.1	2.3	11.5
	16-20	10	40	-	-	-	26.9	1.7	11.5
	21-25	10	-	40	-	-	19.5	<1.0	11.5
	26-30	10	-	-	40	-	22.2	<1.0	11.5
35	CONTROL						63.7	25.4	

Conclusions

A polyacrylate having a molecular weight of about 5,000 (PAA<sup>1</sup>) performs better in the ternary combination than a copolymer of acrylic acid and itaconic acid (PAA<sup>2</sup>) and better than a polyacrylate having a molecular weight of about 10,000 (PAA<sup>3</sup>).

- 60 -

TABLE 15

	<u>Nos.</u>	<u>Deq 2010 (ppm)</u>	<u>ALCO 149 (ppm)</u>	<u>ALCO 175 (ppm)</u>	<u>BEL 161 (ppm)</u>	<u>Sil<sup>1</sup> (ppm)</u>	<u>Ca (ppm)</u>	<u>Mg (ppm)</u>	<u>pH</u>
5	1-5	10	40	-	-	400	23.5	<1.0	11.4
	6-10	10	-	40	-	400	17.8	<1.0	11.4
	11-15	10	-	-	40	400	22.4	<1.0	11.4
10	16-20	10	40	-	-	-	20.3	<1.0	11.3
	21-25	10	-	40	-	-	11.7	<1.0	11.4
	26-30	10	-	-	40	-	23.0	<1.0	-
	CONTROL						60.0	23.7	

15

Conclusions

A polyacrylate having a molecular weight of about 5,000 (PAA<sup>1</sup>; Table 14) performs better in the ternary combination than a polyacrylate having a molecular weight of about 2,000 (Alcosperse 149™), better than a copolymer of acrylic acid and maleic anhydride (Alcosperse 175™), and better than a polyacrylate containing phosphono groups and having a molecular weight of about 4,000 (Belsperse 161™).

25

TABLE 16

	<u>Nos.</u>	<u>Deq 2010 ppm</u>	<u>PAA<sup>2</sup> ppm</u>	<u>Sil<sup>1</sup> ppm</u>	<u>Ca (ppm)</u>	<u>Mg (ppm)</u>	<u>pH</u>
30	1-5	20	80	400	28.9	4.9	11.4
	6-10	20	80	200	26.3	<1.0	11.0
	11-15	20	80	-	26.1	1.8	10.9
	16-20	15	60	400	25.6	<1.0	11.0
35	21-25	15	60	200	27.9	1.3	11.1
	26-30	15	60	-	22.0	<1.0	11.3
	CONTROL				65.3	25.2	

40

Conclusions

A ternary combination employing a copolymer of acrylic acid and itaconic acid having a molecular weight of approximately 8000 (PAA<sup>2</sup>) is ineffective for controlling the precipitation of magnesium and controls the

- 61 -

precipitation of only about one half of the calcium even at relatively high concentrations.

TABLE 17

5	Deq		PAA <sup>1</sup>	Sil <sup>1</sup>	Ca	Mg	pH
	Nos.	2010 ppm			(ppm)	(ppm)	
10	1-5	20	80	400	62.9	22.5	11.3
	6-10	20	80	200	62.1	21.3	11.1
	11-15	20	80	-	63.6	21.4	11.3
	16-20	15	60	400	51.5	14.7	11.2
	21-25	15	60	200	41.1	6.4	11.1
	26-30	15	60	-	40.1	9.3	11.2
15	CONTROL				68.3	23.7	

Conclusions

Various concentrations of Dequest 2010™, PAA<sup>1</sup>, and Sil<sup>1</sup> in the ternary combination provide satisfactory control of both calcium and magnesium. The beneficial effect obtained from incorporation of Sil<sup>1</sup> is demonstrated at the lower levels of Dequest 2010™ and PAA<sup>1</sup>.

TABLE 18

25	Deq		PAA <sup>3</sup>	Sil <sup>1</sup>	Ca	Mg	pH
	Nos.	2010 ppm			(ppm)	(ppm)	
30	1-5	20	80	400	54.7	18.7	1.3
	6-10	20	80	200	51.9	16.8	11.4
	11-15	20	80	-	38.4	8.0	11.4
	16-20	15	60	400	26.6	3.0	11.5
35	21-25	15	60	200	25.6	2.4	11.5
	26-30	15	60	-	26.2	1.2	11.4
	CONTROL				62.4	24.9	

Conclusions

A polyacrylate having an average molecular weight of about 10,000 (PAA<sup>3</sup>) is effective in the ternary combination for controlling both calcium and magnesium when used at higher concentration levels but appears to be less

- 62 -

effective than a polyacrylate having an average molecular weight of about 5,000 (PAA<sup>1</sup>; Table 17).

TABLE 19

<u>Nos.</u>	<u>DCDPP</u> <u>ppm</u>	<u>PAA<sup>1</sup></u> <u>ppm</u>	<u>Sil<sup>1</sup></u> <u>ppm</u>	<u>Ca</u> <u>(ppm)</u>	<u>Mg</u> <u>(ppm)</u>	<u>pH</u>
1-5	10	-	-	3.4	1.0	
6-10	20	-	-	14.3	1.0	
11-15	15	60	-	37.6	21.4	
16-20	15	60	400	52.8	20.3	
21-25	20	80	-	61.3	24.5	
26-30	20	80	400	60.5	23.6	
CONTROL				66.4	25.5	

Conclusions

The phosphonate 1,5-dicarboxy 3,3-diphosphono pentane (DCDPP), performs substantially the same as Dequest 2010<sup>™</sup>. The beneficial effect obtained from incorporation of Sil<sup>1</sup> is demonstrated at the lower levels of Dequest 2010<sup>™</sup> and DCDPP.

TABLE 20

<u>Nos.</u>	<u>Deq</u> <u>2010</u> <u>(ppm)</u>	<u>ALCO</u> <u>175</u> <u>(ppm)</u>	<u>PAA<sup>1</sup></u> <u>(ppm)</u>	<u>Sil<sup>1</sup></u> <u>(ppm)</u>	<u>Ca</u> <u>(ppm)</u>	<u>Mg</u> <u>(ppm)</u>	<u>pH</u>
1-5	20	-	80	400	57.7	21.9	11.4
6-10	10	40	-	400	19.0	1.0	11.4
11-15	20	80	-	400	21.9	1.0	11.5
16-20	-	80	-	400	7.6	4.6	11.5
21-25	20	-	-	400	22.9	1.0	11.4
26-30	-	-	80	400	17.3	23.1	11.4
CONTROL					61.1	23.7	

Conclusions

A ternary combination employing a polyacrylate having an average molecular weight of about 5,000 (PAA<sup>1</sup>) is more effective for controlling both calcium and magnesium than a ternary combination employing a ring opened copolymer of acrylic acid and maleic anhydride having a molecular weight



- 63 -

of about 20,000 (Alcosperse 175™). Ternary combinations employing Alcosperse 175™ are only partially effective for controlling calcium and ineffective for controlling magnesium.

5

TABLE 21

10	<u>Nos.</u>	<u>Deq 2010 (ppm)</u>	<u>7058D (ppm)</u>	<u>PAA<sup>1</sup> (ppm)</u>	<u>Sil<sup>1</sup> (ppm)</u>	<u>Ca (ppm)</u>	<u>Mg (ppm)</u>	<u>pH*</u>
	1-5	15	60	-	400	35.6	9.3	
	6-10	15	60	-	-	28.5	1.5	
	11-15	20	80	-	400	42.0	13.8	
15	16-20	20	80	-	200	38.8	10.2	
	21-25	20	80	-	-	31.5	2.2	
	26-30	20	-	80	400	55.8	23.3	
	CONTROL					61.0	25.8	

20

\* pH after filtration was not determined

Conclusions

A ternary combination employing a polyacrylate having an average molecular weight of about 5,000 (PAA<sup>1</sup>) is more effective for controlling both calcium and magnesium than a ternary combination employing a powdered salt of a granular polyacrylic acid having a molecular weight of about 6000 (Goodright 7058D™). However, it is noted that the inclusion of silicate to the binary combination of Goodright 7058D™ and Dequest 2010™ significantly improves magnesium control.

30

- 64 -

TABLE 22

5	<u>Nos.</u>	<u>Deq2010</u> <u>ppm</u>	<u>PAA<sup>1</sup></u> <u>ppm</u>	<u>Sil<sup>1</sup></u> <u>ppm</u>	<u>Ca</u> <u>(ppm)</u>	<u>Mg</u> <u>(ppm)</u>	<u>pH</u>
	1-5	20	80	400	17.6	10.6	11.5
	6-10	10	40	200	17.0	10.9	11.3
	11-15	5	20	100	16.5	10.5	11.4
10	16-20	2.5	10	50	15.2	2.4	11.4
	21-25	1.25	5	25	9.3	1.0	11.1
	26-30	0.625	2.5	12.5	4.4	1.0	11.2
	CONTROL				17.1	10.9	

15

Conclusions

The ternary combination of Dequest 2010™, PAA<sup>1</sup> and Sil<sup>1</sup> is effective for controlling both calcium and magnesium at reduced concentrations when the concentration of calcium and magnesium has been reduced by softening the water.

20

TABLE 23

25	<u>Nos.</u>	<u>Deq</u> <u>2010</u> <u>(ppm)</u>	<u>CY</u> <u>P-35</u> <u>(ppm)</u>	<u>PAA<sup>1</sup></u> <u>(ppm)</u>	<u>Sil<sup>1</sup></u> <u>(ppm)</u>	<u>Ca</u> <u>(ppm)</u>	<u>Mg</u> <u>(ppm)</u>	<u>pH*</u>
	1-5	20	-	80	400	55.0	21.2	11.4
30	6-10	20	80	-	400	36.1	7.8	11.4
	11-15	20	80	-	-	27.3	2.2	11.4
	16-20	15	60	-	400	25.4	1.6	11.4
	21-25	15	60	-	-	25.2	2.0	11.4
	26-30	-	80	-	400	8.7	19.1	11.4
35	31-35	-	80	-	-	8.6	17.9	11.4
	36-40	-	60	-	-	7.7	13.6	11.2
	CONTROL					57.8	22.2	

40 Conclusions

Cyanamer P-35™, a polyacrylamide, is not as effective as PAA<sup>1</sup> in the ternary combination but does appear to possess some effectiveness for controlling magnesium when used alone.

45

- 65 -

TABLE 24

	Deq 2010	PAA <sup>1</sup>	Sil <sup>2</sup>	Ca	Mg	pH
	<u>Nos.</u>	<u>ppm</u>	<u>ppm</u>	<u>(ppm)</u>	<u>(ppm)</u>	
5	1-5	10	40	400	21.6	1.1 11.6
	6-10	10	40	200	21.9	1.0 11.5
	11-15	15	60	400	40.8	12.8 11.5
	16-20	15	60	200	31.2	5.3 11.6
10	21-25	20	80	400	57.0	22.6 11.5
	26-30	20	80	200	57.6	24.0 11.3
	CONTROL				62.9	25.8

Conclusions

Ortho Silicate ( $\text{Sil}^2$ ) is substantially as effective as RU Silicate ( $\text{Sil}^1$ ) in a ternary system for controlling both calcium and magnesium.

- 5       The specification is presented to aid in the complete non-limiting understanding of our invention. Since many variations and embodiments of the invention can be made without departing from the spirit and scope of our invention, our invention resides in the claims hereinafter  
10   appended.

- 67 -

## WE CLAIM:

1. A solid cast alkaline composition comprising (i) the product obtained by reacting an alkali metal silicate having an  $M_2O:SiO_2$  ratio of less than about 1.5 with an  
5 alkali metal hydroxide in an aqueous environment wherein the  $M_2O:SiO_2:H_2O$  ratio of the product is effective for achieving solidification of the composition under ambient conditions, and (ii) an effective hardness sequestering amount of a threshold system which includes a combination  
10 of a polyacrylic acid or alkali metal salt thereof and an organic phosphonate or alkali metal salt thereof.
2. The composition of claim 1 wherein the reaction product has at least two discrete states of hydration.
3. The composition of claim 1 wherein component (i) of  
15 the composition comprises the product obtained by reacting a sodium hydroxide with a sodium silicate in an aqueous environment.
4. The solid cast alkaline composition of claim 1 further comprising an additional wash chemical.
- 20 5. The composition of claim 4 wherein the additional wash chemical has a characteristic degree of deactivation which increases as the processing temperature increases.
6. The composition of claim 4 wherein the additional wash chemical is selected from a group consisting of a  
25 bleach composition, an enzyme composition, an alkali metal or alkaline earth metal phosphate, an anionic or nonionic surfactant composition and mixtures thereof.
7. The composition of claim 1 wherein the reaction product is obtained by reacting a first alkali metal  
30 silicate having an  $M_2O:SiO_2$  ratio less than 0.8, a second alkali metal silicate having an  $M_2O:SiO_2$  ratio of about 1 to 1.5, and an alkali metal hydroxide in an aqueous environment.
8. The composition of claim 7 wherein the first  
35 alkali metal silicate is present in an amount of about 2 to

- 68 -

about 50 parts per 100 of the cast solid composition.

9. The composition of claim 7 wherein the second alkali metal silicate is present in an amount less than about 30 parts per 100 parts of the cast solid composition.

5 10. The cast solid composition of claim 7 wherein the alkali metal hydroxide is present in an amount from about 1 to about 50 parts per 100 parts of the cast solid composition.

10 11. The solid cast alkaline composition of claim 6 wherein the first alkali metal silicate is a sodium silicate having an  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio of about 0.1 to 0.8 and the second alkali metal silicate is sodium metasilicate.

12. The composition of claim 11 wherein the first type of sodium silicate has a  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio of 0.3 to 0.7.

15 13. The composition of claim 11 wherein about 2 to 50 parts of the sodium silicate having an  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio of about 0.1 to 0.8 was added per 100 parts of a combination of the alkali metal silicate, the alkali metal hydroxide and water to form the cast solid composition.

20 14. The composition of claim 11 wherein less than about 30 parts of the sodium metasilicate was added per 100 parts of a combination of the alkali metal silicate, the alkali metal hydroxide and water to form the cast solid composition.

25 15. The composition of claim 1 wherein there was about 2 to 50 parts of sodium hydroxide added per 100 parts of a combination of the alkali metal silicate, the alkali metal hydroxide and water to form the cast solid composition.

30 16. The composition of claim 11 wherein the threshold system comprises a polyacrylic acid composition or an alkali metal salt thereof and an organic phosphonate composition or an alkali metal salt thereof.

35 17. The composition of claim 1 wherein the threshold system comprises about 2 to 6 parts alkali metal polyacrylic acid per each part alkali metal organic

- 69 -

phosphonate.

18. The composition of claim 1 wherein the polyacrylic acid or alkali metal salt thereof is an alkali metal salt of a polyacrylic acid having a molecular weight of about  
5 2,000 to 8,000.

19. A process for manufacturing an improved solid cast alkaline composition, said process comprising the steps of:

- (a) combining an alkali metal silicate and water to form a process of a fluid reaction mixture; and
- 10 (b) combining the reaction mixture with a wash chemical to form a stable solid reaction product, wherein the reaction product has a characteristic melting point or a decomposition temperature, the reaction product is normally solid at ambient  
15 conditions, and the maximum processing temperature obtained during the formation of the reaction mixture and the reaction product is less than the melting point or decomposition temperature of the reaction product.

20. A process for manufacturing an improved solid cast alkaline composition, said process comprising the step of  
20 reacting an alkali metal silicate with an alkali metal hydroxide in an aqueous environment to form a reaction product having a characteristic melt point or decomposition temperature wherein (i) the  $M_2O:SiO_2:H_2O$  ratio of the  
25 reaction product is effective for achieving solidification of the composition under ambient conditions, (ii) a maximum processing temperature is attained during formation of the reaction product, and (iii) the melt point or decomposition temperature of the reaction product is greater than the  
30 maximum processing temperature.

21. The process of claim 20 further comprising the step of blending an additional wash chemical into the reaction product.

22. The process of claim 21 wherein the additional wash  
35 chemical has a characteristic degree of deactivation which

- 70 -

increases as the processing temperature increases.

23. The process of claim 21 wherein the additional wash chemical is selected from the group consisting of bleach composition, an enzyme composition, an alkali metal or alkaline earth metal phosphate, an anionic and nonionic surfactant composition and mixtures thereof.

24. A process for manufacturing an improved solid cast alkaline composition, said process comprising the steps of (i) blending an effective hardness sequestering amount of a threshold system comprising a polyacrylic acid and an organic phosphonate into an aqueous reaction mixture of an alkali metal silicate and an alkali metal hydroxide, and (ii) reacting the alkali metal silicate and alkali metal hydroxide in the reaction mixture to form a reaction product having a characteristic melt point or decomposition temperature above 50°C; wherein (i) the  $M_2O:SiO_2:H_2O$  ratio of the reaction product is effective for achieving solidification of the composition under ambient conditions, (ii) a maximum processing temperature is attained during formation of the reaction product, and (iii) the melt point or decomposition temperature of the reaction product is greater than the maximum processing temperature.

25. The process of claim 24 wherein the threshold system includes about 2 to 6 parts of the polyacrylic acid or alkali metal salt thereof for each part of the organic phosphonate or alkali metal salt thereof.

26. The process of claim 24 wherein there is about 0.2 to 2.0 parts of the threshold system for each part of alkali metal silicate in the reaction product.

27. The process of claim 24 wherein the polyacrylic acid or alkali metal salt thereof has a molecular weight of about 2,000 to 8,000.

28. The process of claim 20 wherein a sodium silicate, a sodium hydroxide and water are combined to form the



- 71 -

reaction mixture.

29. The process of claim 20 wherein the relative amounts of alkali metal silicate, alkali metal hydroxide and water incorporated into the composition are effective  
5 for producing a reaction product having about 20 to 45 parts water per 100 parts of a combination of the alkali metal silicate, the alkali metal hydroxide and water in the cast solid composition and an  $M_2O:SiO_2$  ratio of about 1.0 to 2.5.

10 30. The process of claim 20 wherein the relative amounts of alkali metal silicate, alkali metal hydroxide and water incorporated into the composition are effective for producing a reaction product having about 20 to 50 parts water per 100 parts of a combination of the alkali  
15 metal silicate, the alkali metal hydroxide and water in the cast solid composition and an  $M_2O:SiO_2$  ratio of about 2.5 to 4.0.

31. The process of claim 20 wherein the relative amounts of alkali metal silicate, alkali metal hydroxide  
20 and water incorporated into the composition are effective for producing a reaction product having about 20 to 40 parts water per 100 parts of a combination of the alkali metal silicate, the alkali metal hydroxide and water in the cast solid composition and an  $M_2O:SiO_2$  ratio of about 2.5  
25 to 4.0.

32. The process of claim 20 wherein the relative amounts of alkali metal silicate, alkali metal hydroxide and water incorporated into the composition are effective  
for producing a reaction product having about 20 to 45  
30 parts water per 100 parts of a combination of the alkali metal silicate, the alkali metal hydroxide and water in the cast solid composition and an  $M_2O:SiO_2$  ratio of about 2.5 to 3.5.

33. The process of claim 20 wherein the maximum  
35 process temperature attained is at least 10 C less than the

- 72 -

melting point or decomposition temperature of the reaction product.

34. The process of claim 20 wherein the melting point or decomposition temperature of the reaction product is greater than about 50°C.

35. The process of claim 20 wherein the melting point or decomposition temperature of the reaction product is greater than about 65°C.

36. The process of claim 20 further comprising the step of placing the reaction product in a packaging container prior to solidification.

37. The process of claim 20 wherein the additional wash chemical has a characteristic degree of deactivation which increases as the processing temperature increases.

38. The composition of claim 4 wherein the additional wash chemical is an alkali metal or alkaline earth metal phosphate.

39. A solid cast alkaline composition comprising the product obtained by reacting an alkali metal silicate having an  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio of less than about 1.5 with an alkali metal hydroxide in an aqueous environment wherein the cast solid composition has (i) a final water content of about 20 to about 45 wt% with an  $\text{M}_2\text{O}:\text{SiO}_2$  ratio of about 1 to 2.5 or a water content of about 20 to about 50 wt% with an  $\text{M}_2\text{O}:\text{SiO}_2$  ratio of 2.5 to 4, and (ii) a melt/decomposition temperature of at least 50°C.

40. The composition of claim 39 wherein the alkali metal silicate is sodium silicate and the alkali metal hydroxide is sodium hydroxide.

41. The composition of claim 39 further comprising a threshold system of an alkali metal polyacrylic acid and an alkali metal organic phosphonate.

42. The composition of claim 41 wherein the threshold system includes about 2 to 6 parts alkali metal polyacrylic acid per each part alkali metal organic phosphonate.

- 73 -

43. The composition of claim 42 wherein the alkali metal polyacrylic acid has a molecular weight of about 2,000 to 8,000.

44. A solid cast alkaline composition comprising the product obtained by reacting an alkali metal silicate having an  $M_2O:SiO_2$  ratio of less than about 1.5 with an alkali metal hydroxide in an aqueous environment wherein the cast solid composition has (i) a final water content of about 20 to about 40 wt% with an  $M_2O:SiO_2$  ratio of about 1.5 to 2.5 or a water content of about 20 to about 45 wt% with an  $M_2O:SiO_2$  ratio of 2.5 to 3.5, and (ii) a melt/decomposition temperature of at least 50°C.

45. The composition of claim 44 wherein the alkali metal silicate is sodium silicate and the alkali metal hydroxide is sodium hydroxide.

46. The composition of claim 44 further comprising a threshold system of an alkali metal polyacrylic acid and an alkali metal organic phosphonate.

47. A process for manufacturing an improved solid cast alkaline composition, said process comprising the step of reacting an alkali metal silicate with an alkali metal hydroxide in an aqueous environment to form a thermodynamically unstable substantially fluid reaction product wherein (i) the  $M_2O:SiO_2:H_2O$  ratio of the reaction product is effective for achieving solidification of the composition under ambient conditions, and (ii) the fluid reaction product solidifies to a thermodynamically stable solid block substantially simultaneously throughout the entire cross section thereof.

48. The process of claim 20 wherein the alkali metal silicate comprises a first alkali metal silicate having an  $M_2O:SiO_2$  ratio of less than 0.8 and a second alkali metal silicate having an  $M_2O:SiO_2$  ratio of about 1 to 1.5.

49. The process of claim 48 wherein the first alkali metal silicate is a sodium silicate having an  $Na_2O:SiO_2$

- 74 -

ratio of about 0.1 to 0.8 and the second alkali metal silicate is sodium metasilicate.

50. A substantially homogeneous solid cast alkaline composition comprising the product obtained by reacting an  
5 alkali metal silicate with an alkali metal hydroxide in an aqueous environment wherein the cast solid composition has an  $M_2O:SiO_2$  ratio of 1 to 4 and a melt/decomposition temperature of at least 50°C.

51. The composition of claim 50 wherein the alkali  
10 metal silicate is sodium silicate and the alkali metal hydroxide is sodium hydroxide.

52. The composition of claim 50 further comprising a threshold system of an alkali metal polyacrylic acid and an alkali metal organic phosphonate.

15 53. The composition of claim 52 further comprising an additional wash chemical.

54. The composition of claim 53 wherein the additional wash chemical is an alkali metal or alkaline earth metal phosphate.

20 55. A substantially homogeneous solid cast alkaline composition comprising the product obtained by reacting an alkali metal silicate with an alkali metal hydroxide in an aqueous environment wherein the cast solid composition has an  $M_2O:SiO_2$  ratio of 1.5 to 3.5 and a melt/decomposition  
25 temperature of at least 100°C.

56. The composition of claim 55 wherein the alkali metal silicate is sodium silicate and the alkali metal hydroxide is sodium hydroxide.

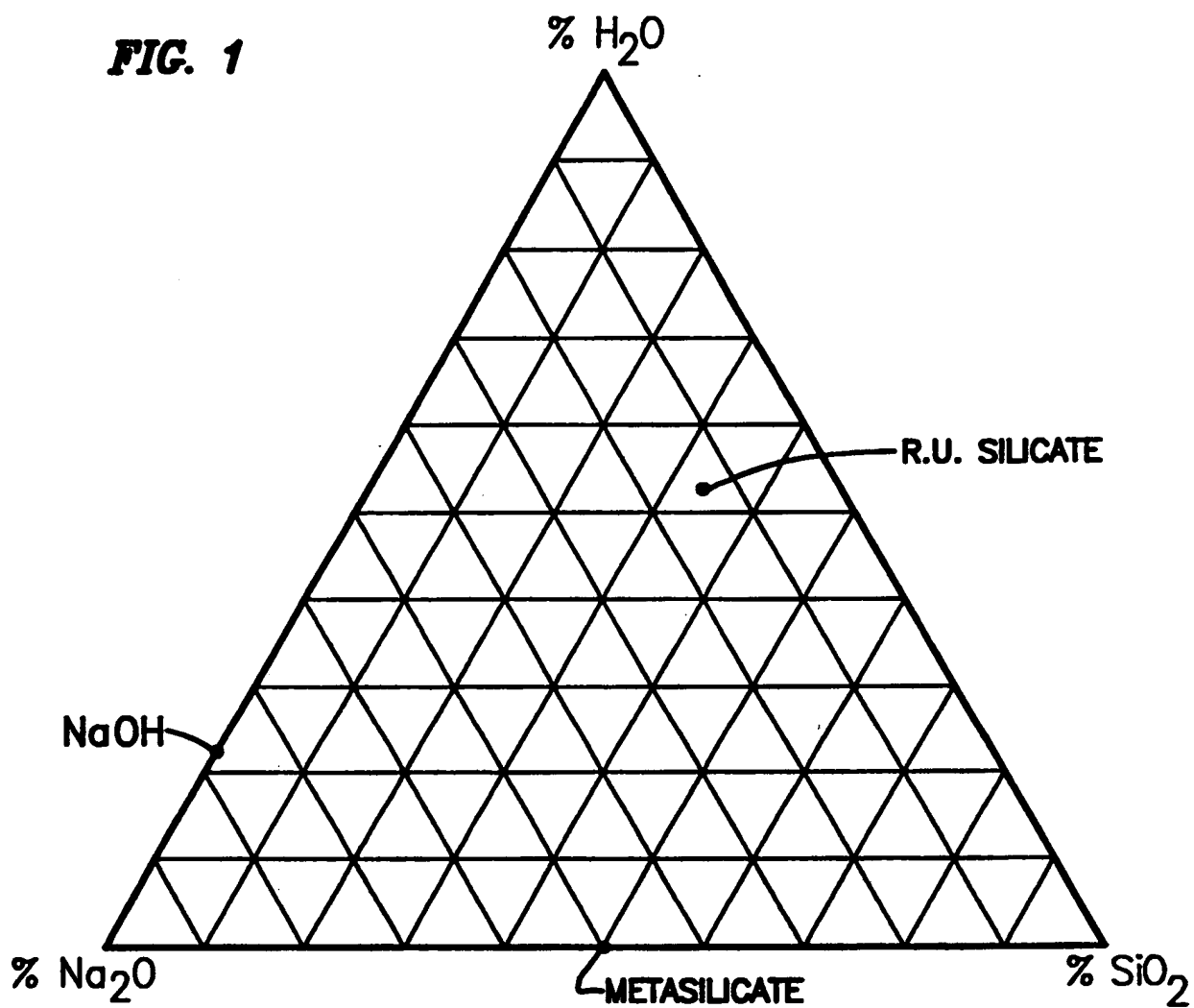
57. The composition of claim 55 further comprising a  
30 threshold system of an alkali metal polyacrylic acid and an alkali metal organic phosphonate.

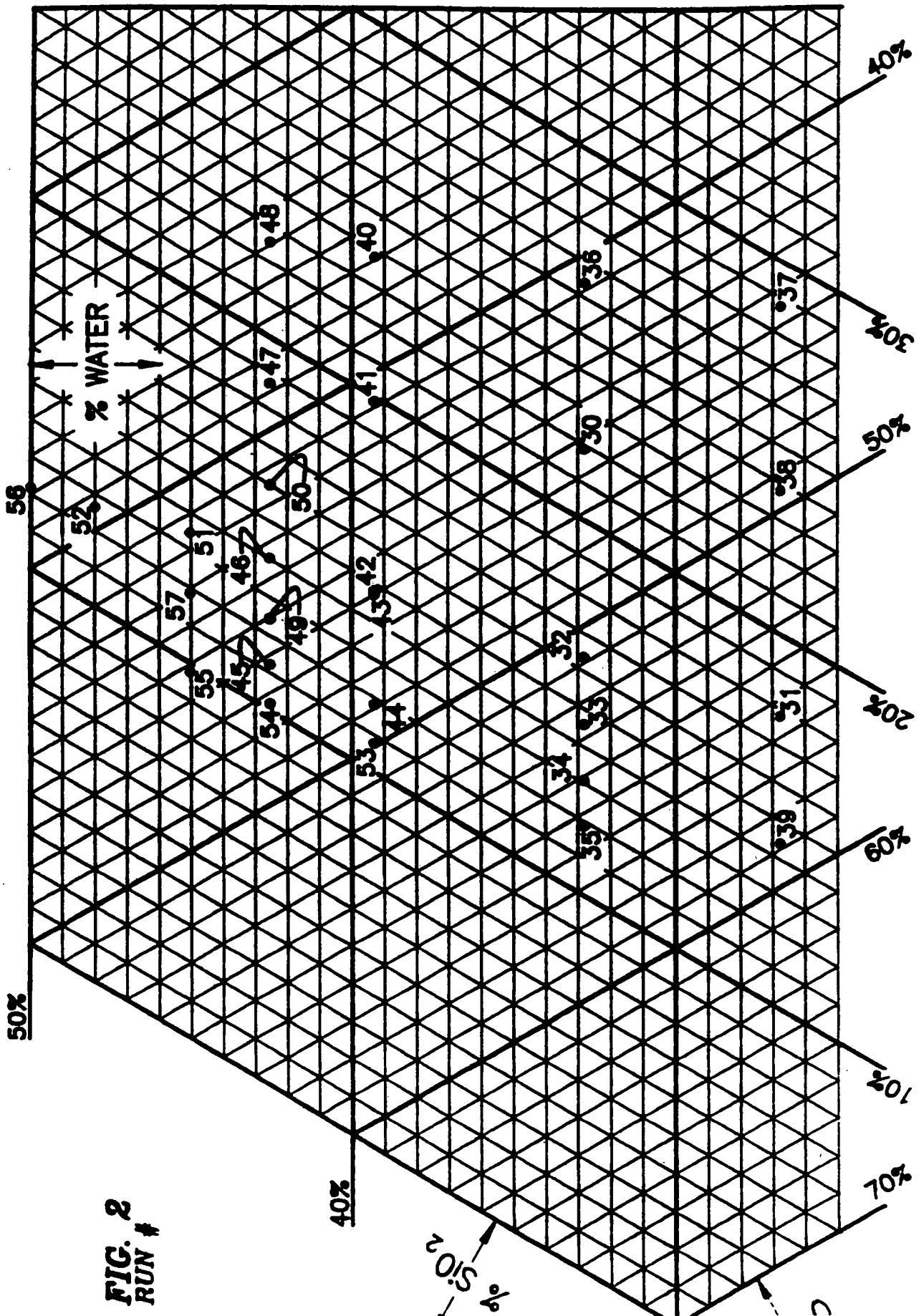
58. The composition of claim 55 further comprising an additional wash chemical.

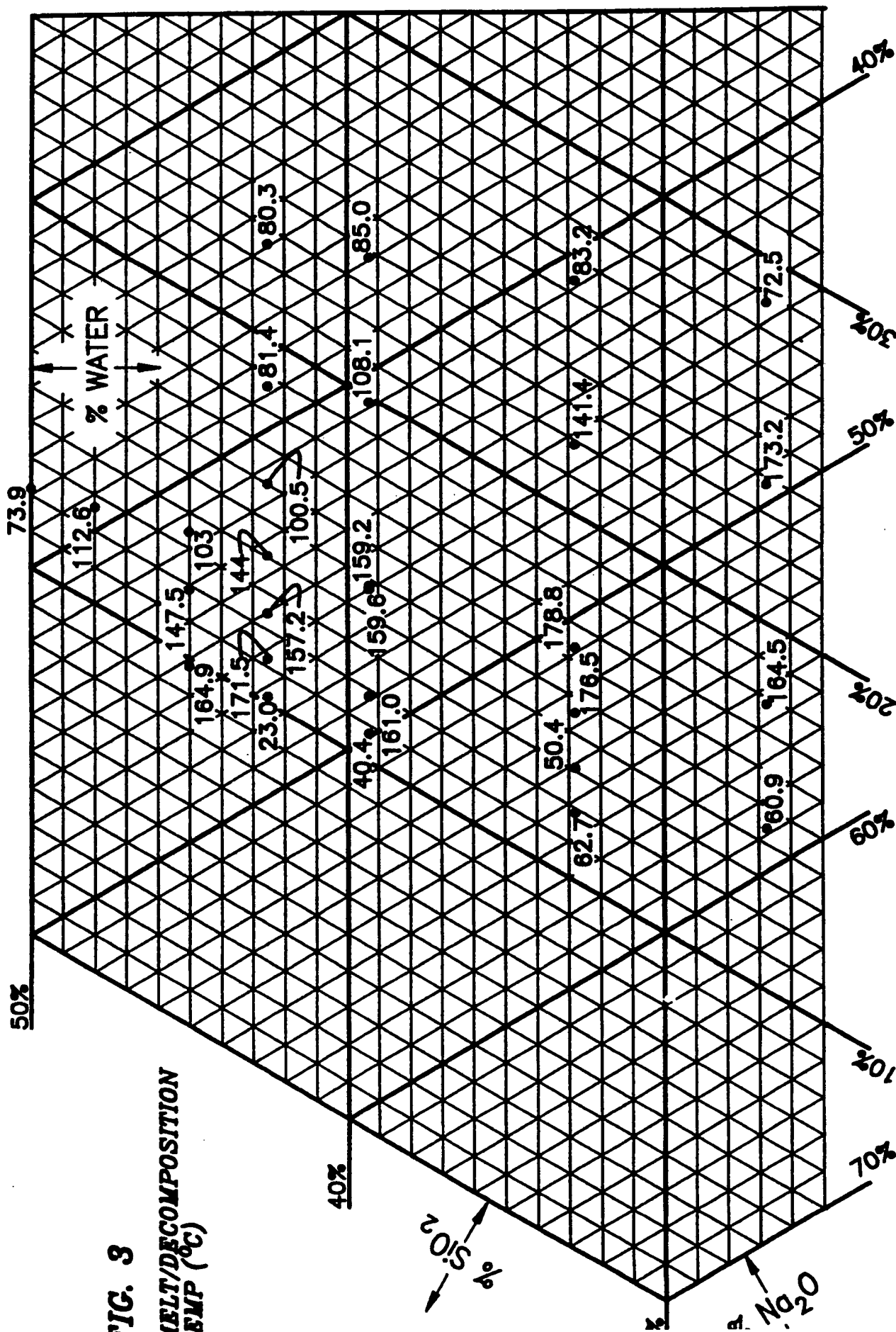
59. The composition of claim 55 wherein the additional  
35 wash chemical is an alkali metal or alkaline earth metal

- 75 -

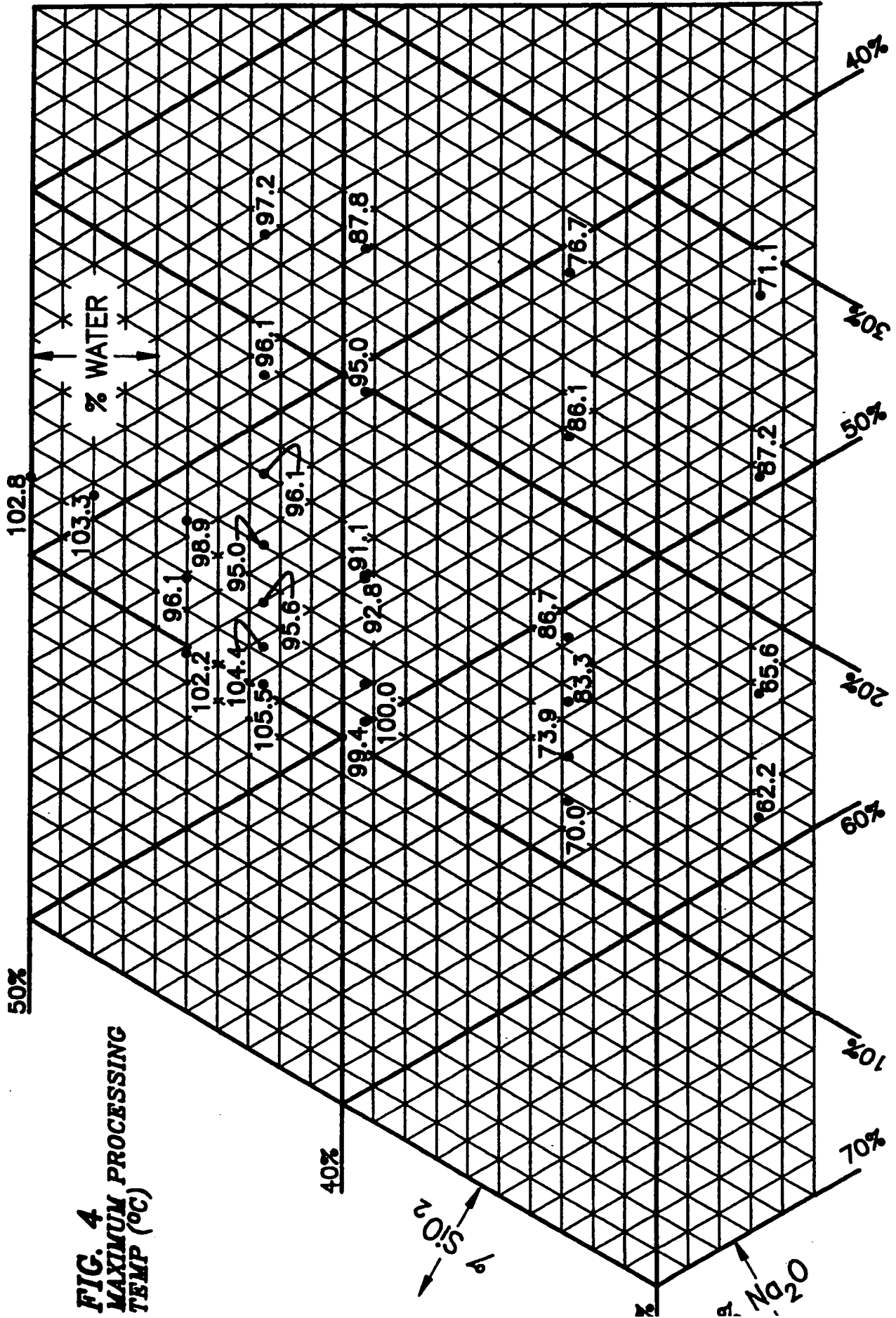
phosphate.

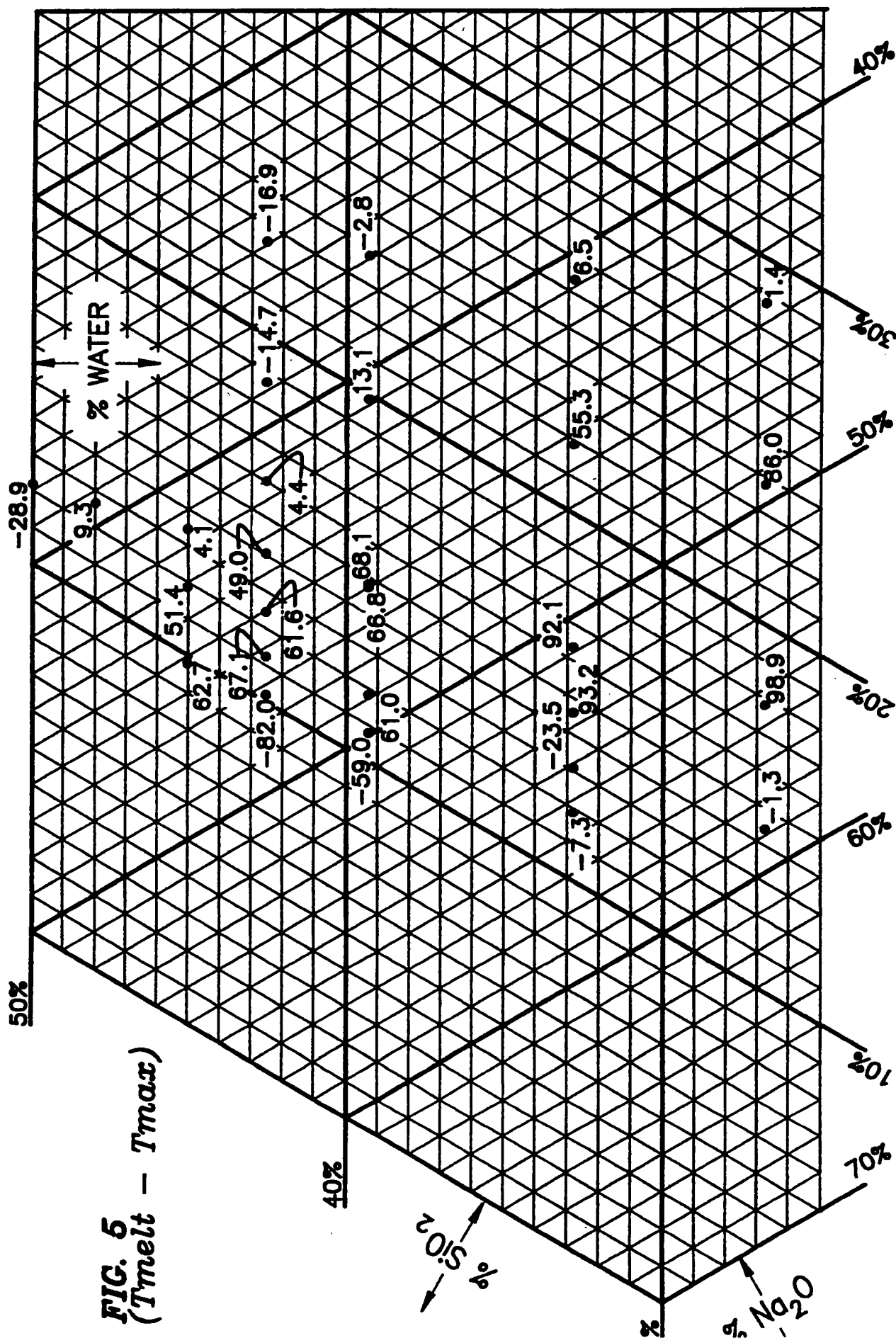
**FIG. 1**

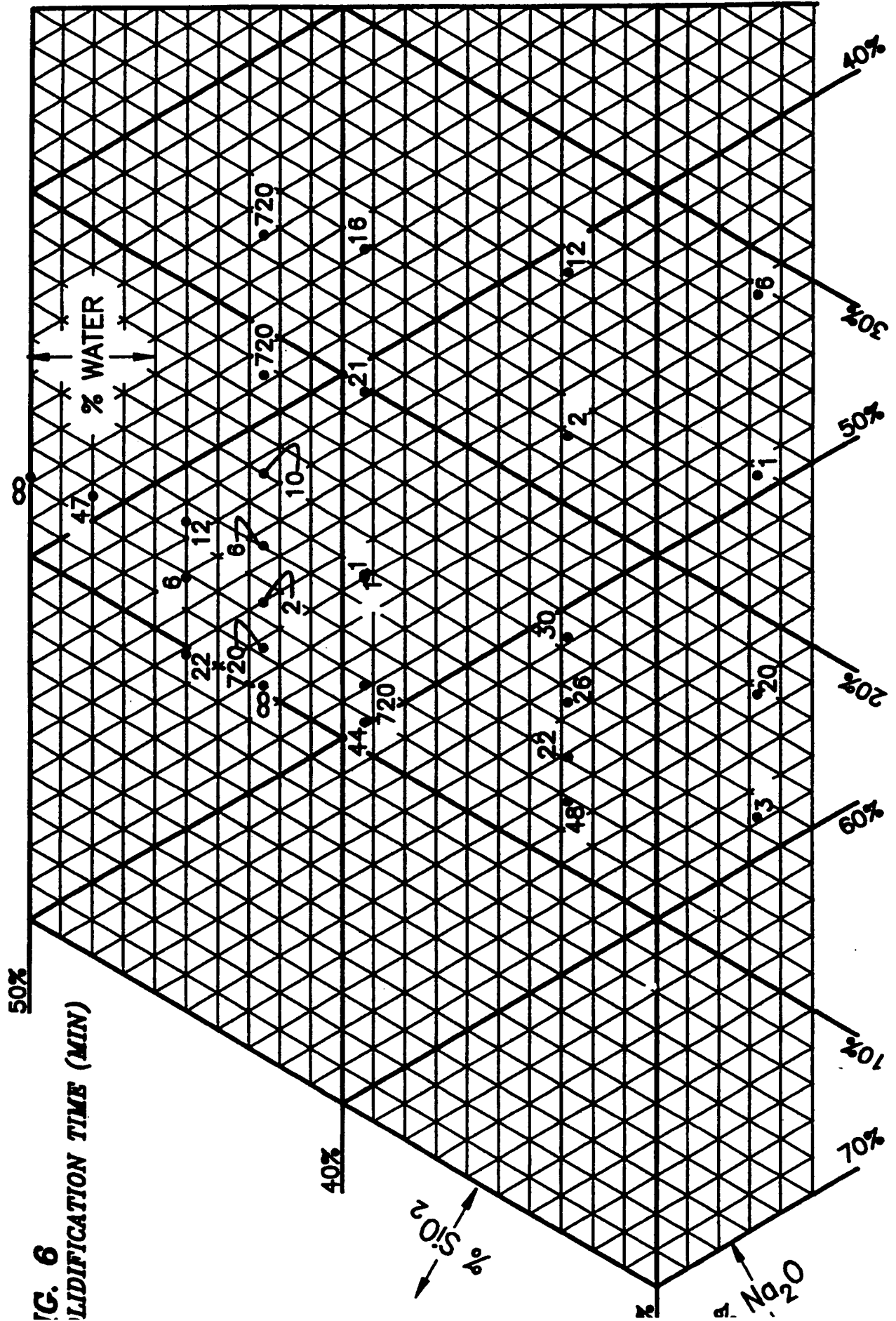












## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 92/00492

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C11D17/00; C11D3/08; C11D3/37		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C11D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claims No. <sup>13</sup>
A	EP,A,0 178 893 (ECOLAB INC.) 23 Apr11 1986  see claims 1-11 ---	1,4,6, 19,38, 39,44, 47,50, 53-55, 58,59
A	WO,A,9 012 081 (ECOLAB INC.) 18 October 1990  see claims 1,12,13,16-24 ----- -/-	1,3,4,6, 11,16, 38-41, 44-46, 50-59
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
29 MAY 1992	22. May 92	
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer SERBETSOGLOU A. <i>[Signature]</i>	

## III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category <sup>o</sup>	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,4 753 755 (R.E. GANSSE) 28 June 1988 cited in the application  see the whole document ---	1,3,4,6, 16,19, 39-41, 44-47, 50-52, 55-57
A	EP,A,0 264 043 (HENKEL) 20 April 1988  see column 5, line 5 - line 16; claim 1; examples ---	1,19,39, 50-52, 55-57

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9200492  
SA 56550

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 29/05/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0178893	23-04-86	US-A- 4595520	17-06-86
		AU-B- 573897	23-06-88
		AU-A- 4734385	24-04-86
		CA-A- 1259543	19-09-89
		DE-A- 3585261	05-03-92
		JP-A- 61098799	17-05-86
		US-A- 4680134	14-07-87
WO-A-9012081	18-10-90	AU-A- 4051289	05-11-90
		EP-A- 0465461	15-01-92
US-A-4753755	28-06-88	None	
EP-A-0264043	20-04-88	DE-A- 3634812	14-04-88
		DE-A- 3777318	16-04-92
		US-A- 5064554	12-11-91